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Final Report

DELAMINATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

by

William J. Corbett and John H. Burson, III

Prepared for

THE DIVISION OF ISOTOPES DEVELOPMENT
UNITED STATES ATOMIC ENERGY COMMISSION

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ABSTRACT

The objective of the research performed under this project was to investigate the possibilities of reducing large particles of kaolin to small plate-like particles with high-energy, ionizing radiation, and to investigate the changes in the physical and colloidal properties of kaolin due to the effects of high-energy, ionizing radiation.

Two different kaolins from the Cretaceous Tuscaloosa formation in Georgia were used in these studies. The kaolins differed in degree of crystallinity, particle size, and extent of processing before irradiation. Samples of these kaolins were exposed to doses of 0.667 Mev gamma-radiation ranging from 10^{18} to 10^{22} electron-volts per gram. Significant changes were observed in the degree of crystallinity, specific surface area, cation exchange capacity and slurry viscosity. Delamination of the larger particles into smaller platelike particles was detected for one of the samples, but not the other. Some unusual alterations in the appearance of the surface were found for a significant portion of the particles examined. Indications of a decrease in the ratio of hydrogen bonded to unbonded hydroxyl groups were detected by infrared absorption. Samples of irradiated kaolin appeared to grind more readily than did the unirradiated.

The changes in physical and chemical properties are discussed in terms of the observed atomic displacements produced in the kaolinite structure by the gamma-radiation. Recommendations for future research are presented.

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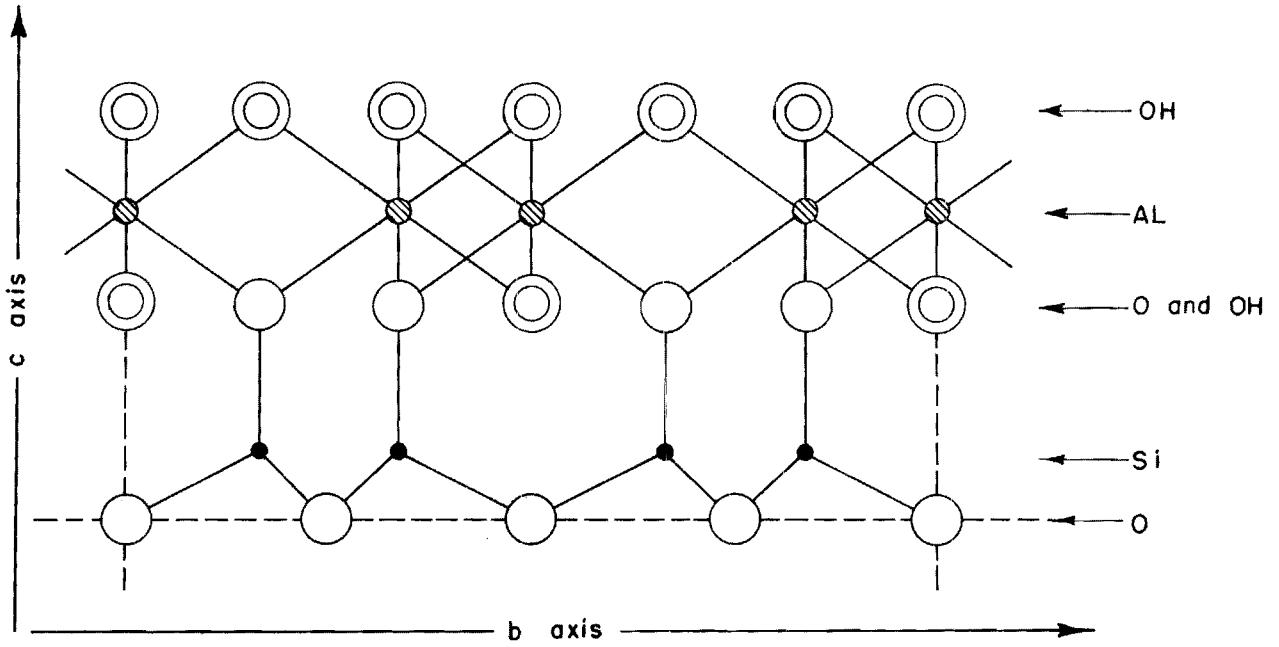
I. INTRODUCTION

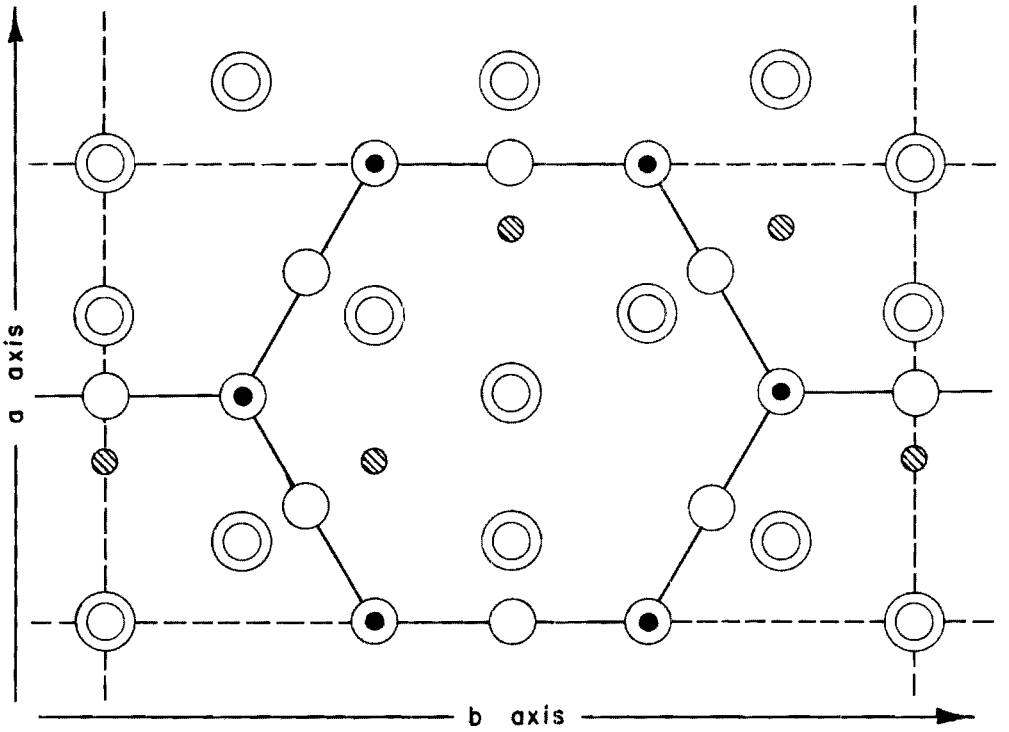
This report summarizes the work performed from April 1, 1959, to March 31, 1961. The objective of the research performed under this project was to investigate the possibilities of reducing large particles of kaolin to small plate-like particles with high-energy, ionizing radiation, and to investigate the changes in the physical and colloidal properties of kaolin due to the effect of high-energy, ionizing radiation.

The structure of the kaolin layer is shown in Figure 1. Figure 1a is a diagrammatic representation of the layer viewed from the side. The base plane is a sheet of oxygen atoms linked to silicon atoms in the sheet immediately above. The third sheet contains both oxygen atoms, which are connected to the silicon atoms of the second sheet, and hydroxyl groups, linked to the aluminum atoms of the sheet above. The aluminum atoms are also linked to a sheet of closely packed hydroxyl groups which comprise the fifth, and final, sheet of the layer. Each silicon atom is bound to three oxygen atoms of the base sheet and one oxygen atom of the third sheet in a tetrahedral coordination. The aluminum atoms form an octahedral coordination with two oxygens and a hydroxyl group of the third sheet and three hydroxyl groups of the fifth sheet. It can be seen from the diagrammatic representation of the view down into the layer (Figure 1b) that only two-thirds of the available sites are occupied by aluminum atoms. This is necessary for the structure to be electrically neutral.

The thickness of the layer is 4.31 angstroms; the layer has no unsatisfied bonds in the top and bottom sheets of atoms. The unit layer extends 8.93 angstroms along the b axis and 5.14 angstroms along the a axis. However, the unit can extend itself indefinitely along the a and b axes since



A. SIDE VIEW



B. TOP VIEW (001 PLANE)

Figure 1. The Kaolin Layer.

it has unsatisfied valence bonds at the edges.

The above structure is known as the kaolin layer because it is the basic structure of minerals belonging to the kaolin group. Some of these minerals are kaolinite, nacrite, dickite, endellite, and halloysite. These minerals differ primarily in the number of kaolin layers per unit cell. Kaolinite contains one layer per unit cell, nacrite six layers per unit cell, dickite two layers per unit cell, endellite one layer plus four layers of water molecules per unit cell,[1] and halloysite one layer plus one layer of water molecules per unit cell.[2] The term kaolin is usually used to describe a clay which contains one or more of the above minerals as a primary constituent.

Since the unit layer is common to all the kaolin minerals, their $\underline{a}_o$ and $\underline{b}_o$ dimensions are all very similar. The dimension of a unit cell along the $\underline{c}$ axis is determined by the relative positions of the aluminum atoms in successive kaolin layers. For example, if two layers are placed directly above one another, the oxygen atoms of the lowest sheet in one layer will lie on a vertical line with the similar atoms in the next layer. The same holds true for the silicon atoms in the adjacent layers and for the hydroxyl atoms. This does not necessarily hold true for the aluminum atoms. There are six possible locations for the four aluminum atoms in a layer, which means for a given arrangement of aluminum atoms in one

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[1] S. B. Hendricks, "On the Crystal Structure of Clay Minerals: Dickite Halloysite and Hydrated Halloysite," Am. Mineral. 23, 295-301 (1938).

[2] S. B. Hendricks and M. E. Jefferson, "Structures of Kaolin and Talc-Pyrophyllite Hydrates and their Bearing on Water Sorption of Clays," Am. Mineral. 23, 863-875 (1938).

layer there are three alternate arrangements of these atoms in the next layer. Addition of successive layers introduces additional complications. The relative position and arrangement of succesive layers depends on the orientation of the oxygen atoms and hydroxyl layers of adjacent layers. One stable configuration is achieved when the layers are placed directly above each other. The angles α and β, which represent the angle between the c axis and the b and a axes are 90°, respectively. This arrangement is closely obtained in the rare mineral nacrite. Certain displacements of one layer relative to another can also result in a stable arrangement of O-HO linking. These displacements are distances of $ma_o/6$ of $nb_o/6$, along the a and b axis, respectively, where m and n are integers and a_o and b_o are the cell dimensions. The values of these shifts and the resulting angles have been determined and are well documented.[3,4]

The general structural characteristics of the kaolin minerals are in accord with these principles. The a_o and b_o dimensions of the unit cells are all very similar since the kaolin layer is common to all. The c_o dimension is determined by the type of stacking and the arrangement of aluminum atoms in successive layers. The angular relationship of the c axis to the a and b is governed by the relative displacements of the layers.

Kaolinite, the most common form of kaolin, forms plate-like, pseudo-hexagonal crystals whose thickness is very small in comparison with their length and breadth. Individual crystals of kaolinite usually occur in

[3] G. W. Brindley, X-ray Identification and Crystal Structures of Clay Minerals, (London: The Mineralogical Society, 1951).

[4] A. B. Searle and R. W. Grimshaw, The Chemistry and Physics of Clays, (Third Edition; London: Ernest Benn Ltd., 1959).

the colloidal size range, and they vary from a few thousandths to a few tenths of a micron in thickness. It is obvious, therefore, that an individual crystal must be several unit cells thick. Since the kaolin layer has no unsatisfied valence bonds on the faces parallel to the a and b axes, interlayer bonding is accomplished by van der Waals forces and long hydrogen bonds.

Frequently, kaolin is found to contain very large particles that appear to be laminates of individual kaolinite crystals. Such a particle, or stack, is shown in Figure 2. These large particles range in size from 2 microns to greater than 40 microns equivalent spherical diameter. The terms "stack" or "booklets," which are often used to describe these particles because of the resemblance in appearance to a stack of cards or the edges of the pages in a closed book, are very apt from the standpoint of appearance, but misleading in terms of structure. Rather than aggregates of individual plate-like kaolinite crystals, these particles are actually homogeneous, crystalline solids that contain a number of kaolinite crystallites. Due to their crystal habit, these crystallites are preferentially oriented in a laminar manner, and the etch pits that occur at the interfaces between these crystallites give rise to the serrated surfaces which produce the effect of an aggregate of individual plates. This effect is further enchanced by the fact that the crystallites have a thickness equivalent to that of the individually occurring kaolinite crystals. In fact, experiments with devices capable of exerting very high shearing forces parallel to the crystallite interfaces have produced individual plates of sizes comparable to naturally occurring plates. This is not surprising, since any plane perpendicular to the c crystallographic

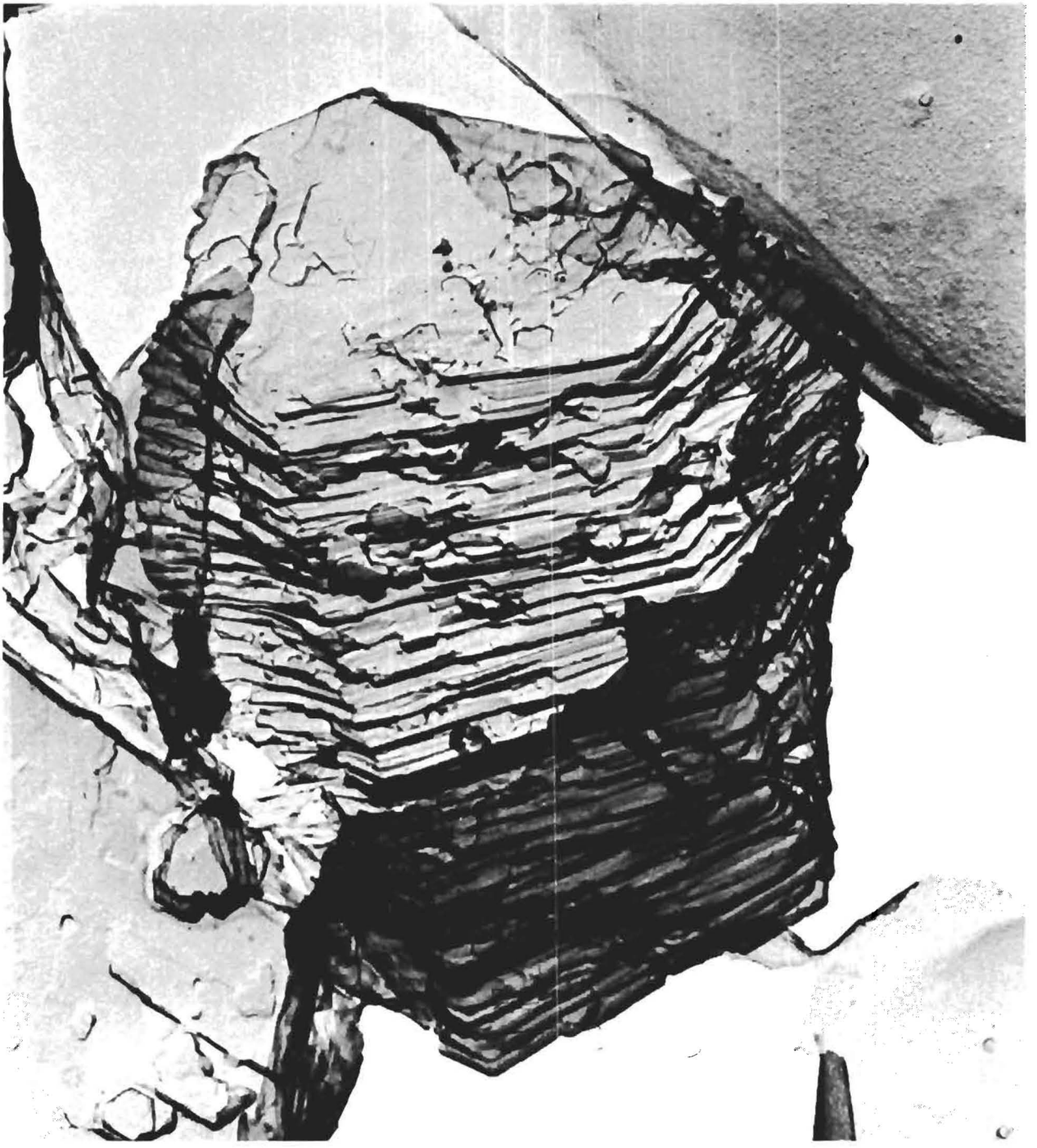

Figure 2. Electron Micrograph of a Typical Kaolin Stack (14,800X).

axis represents a plane of cleavage and the interfaces are no doubt the areas of greatest weakness within the large particles.

The presence of stacks in kaolin is very undesirable from an economic viewpoint. The presence of individual colloidal-sized plates is the very characteristic which endows kaolin with some of its most valuable commercial properties. Ordinary size reduction techniques are unable to produce colloidal-sized plates from stacks.

II. EXPERIMENTAL WORK

All the experimental work on this project was performed with kaolins whose primary constituent was the mineral kaolinite. One of these kaolins came from a deposit in Washington County, Georgia. This kaolin was fractionated after mining until 95 per cent of the material, by weight, had a particle size above 2 microns equivalent spherical diameter. The other sample of kaolin used in these studies came from a kaolin deposit in Twiggs County, Georgia. This kaolin received no treatment after mining, and the material contained 85 per cent, by weight, of particles above 2 microns equivalent spherical diameter. Since kaolin particles with equivalent spherical diameters greater than 2 microns represent stacks,[5] these kaolins both contained a large proportion of stacks on a weight basis. The kaolins received no further treatment before irradiation except a short drying period of 4 to 6 hours at 110°C.

A. Irradiation of Samples

The gamma irradiation of kaolin was accomplished using the Georgia Tech 12,000-curie Cesium-137 Research Irradiator. This irradiator is of the Notre Dame type, and an average dose rate of 7.5×10^{19} electron-volts per gram per hour is obtainable in the center well. The maximum dose rate obtainable in the center well is 8.75×10^{19} electron-volts per gram per hour, and this maximum uniform dose is available over a vertical height of 3 inches. All irradiations performed with the Research Irradiator were made in the center well.

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[5] J. H. Koenig and S. C. Lyons, "Correlation of Kaolinite Crystal Shape With Particle Size and Some Effects on Ceramic Behavior," Ceramic Age 66, No. 1, 8-14 (1955).

Radiation doses ranging from 10^{18} to 10^{22} electron-volts per gram were employed in this work. Two different procedures, utilizing two different sample holders, were employed for sample irradiation. In one of these two procedures a large pyrex test tube was used as a sample holder. Approximately 100 grams of kaolin were placed in this test tube and irradiated in the center well of the irradiator. The samples were therefore located in the entire region of radiation flux and the dose received by the sample was calculated from the average dose rate of the center well. This dose was determined by integration of the area under a dose-rate-versus-vertical-height curve which had been obtained for the Research Irradiator by other investigators.[6] When the samples were removed from the irradiator they were thoroughly mixed to compensate for the nonuniformity of dose rate over the vertical length of the sample holder. Irradiations were also performed using a sample holder consisting of an aluminum cylinder, with a wall thickness of approximately 1/8 inch, divided into two compartments by a partition perpendicular to its cylindrical axis, and closed at either end by threaded aluminum plugs. These compartments held between 10 and 15 grams each. The cylinder, which was 5-1/4 inches long, was placed on a spacer within the sample carrier of the Cesium-137 Research Irradiator. This spacer located the sample holder only in the region of uniform radiation flux. In addition to providing a more uniform dose rate, this procedure allowed samples of two different kaolins to be irradiated simultaneously.

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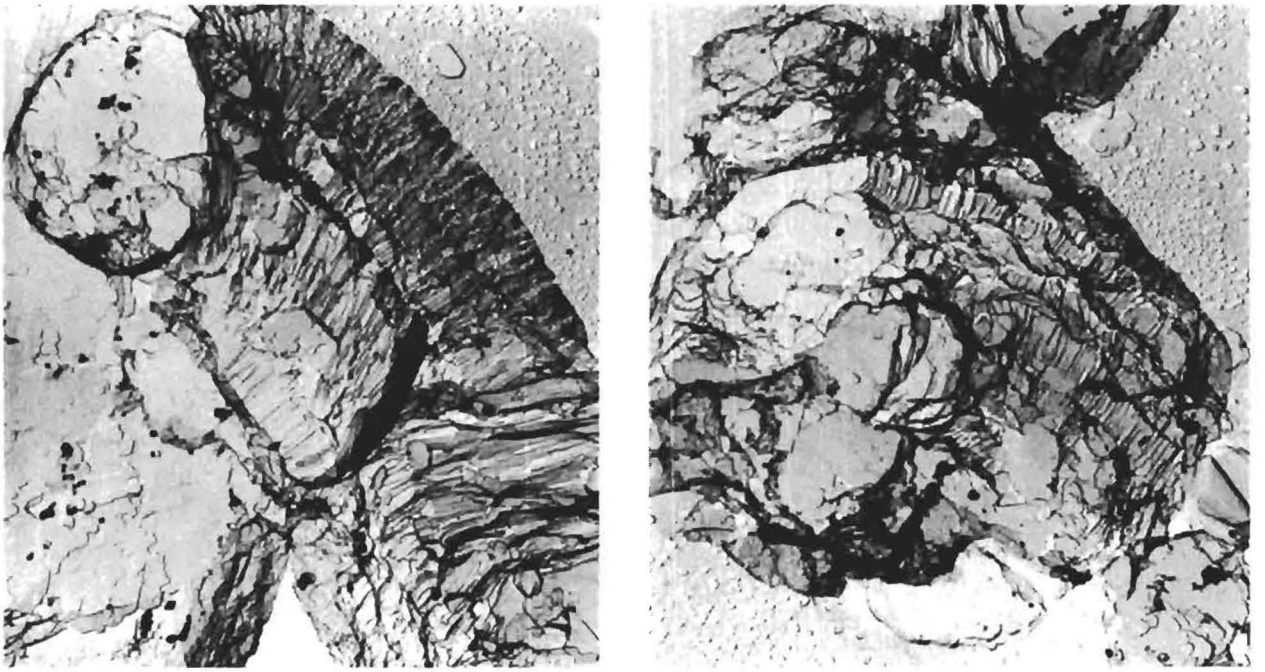
[6] R. C. Palmer and R. W. Carter, "A High Intensity Cesium-137 Research Irradiator," International Journal of Applied Radiation and Isotopes 9, 123-24 (1960).

The temperature of the samples during irradiation was determined by placing a copper-constantan thermocouple in the center of a sample contained in the pyrex tube and automatically recording the temperature as a function of time. The temperature was found to rise uniformly from room temperature (approximately 70° F) to 100° F in a period of 15 to 20 minutes. The temperature remained constant at 100° F during the remainder of the irradiation.

B. Electron Microscopy

Unirradiated and irradiated samples of both kaolins were examined qualitatively by electron microscopy. The particles were replicated by depositing a thin film of platinum and carbon on them, in a vacuum chamber, from an arc. The particles were removed from the film by dissolution with hydrofluoric acid, and micrographs were obtained from these replicas with an electron microscope. These replicas show much greater surface detail when observed with the electron microscope than when the particles are observed directly. The field of view of the electron microscope was not large enough to contain a sufficient number of particles, the size of those found in the kaolin samples, to provide a very representative estimate of the particle-size distribution. The Washington County kaolin did appear to contain more small, plate-like particles after irradiation although a large number of stacks remained. The appearance of the micrographs of the Twiggs County kaolin was quite similar before and after irradiation. Typical micrographs of these two kaolins are shown in Figures 3 and 4.

Some unusual physical surface appearance was observed in a number of the micrographs. In Figures 5 and 6, for example, an unusual etched appearance can be seen on the edges of the kaolinite crystallites composing



UNIRRADIATED

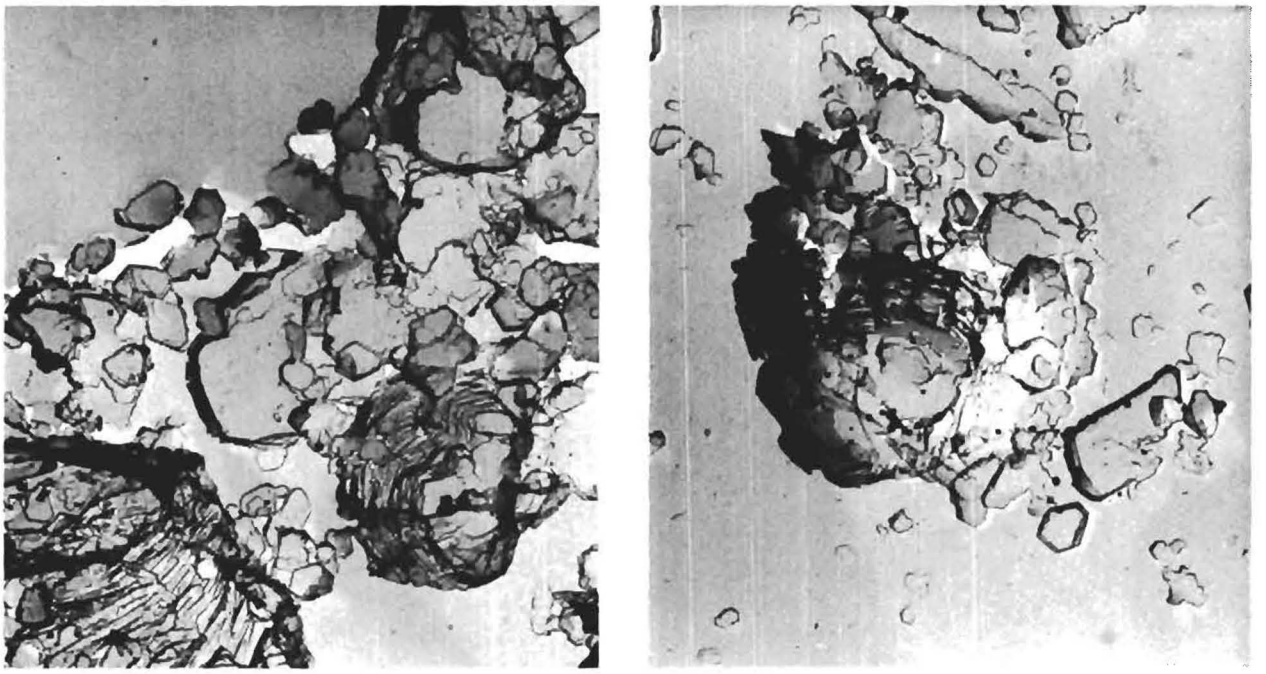


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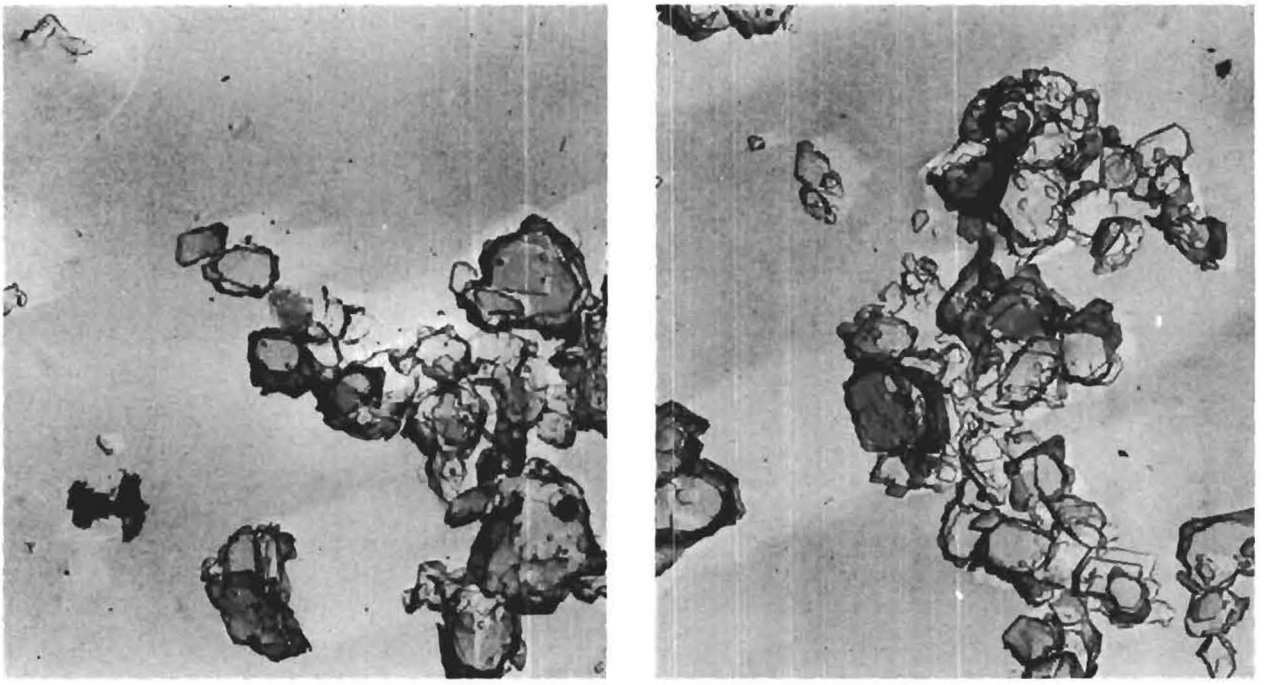
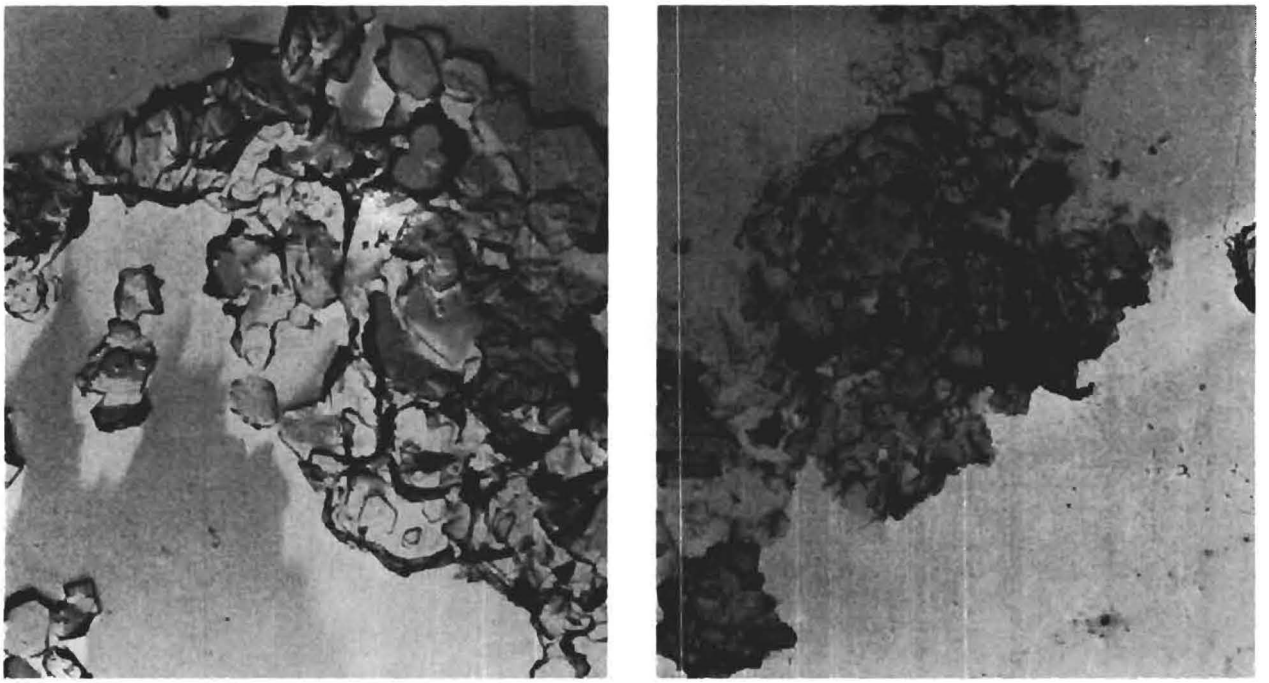
Figure 3. Electron Micrographs of Washington County Kaolin Before and After Irradiation (7,400X).



UNIRRADIATED



IRRADIATED

Figure 4. Electron Micrographs of Twiggs County Kaolin Before and After Irradiation (7,200X).

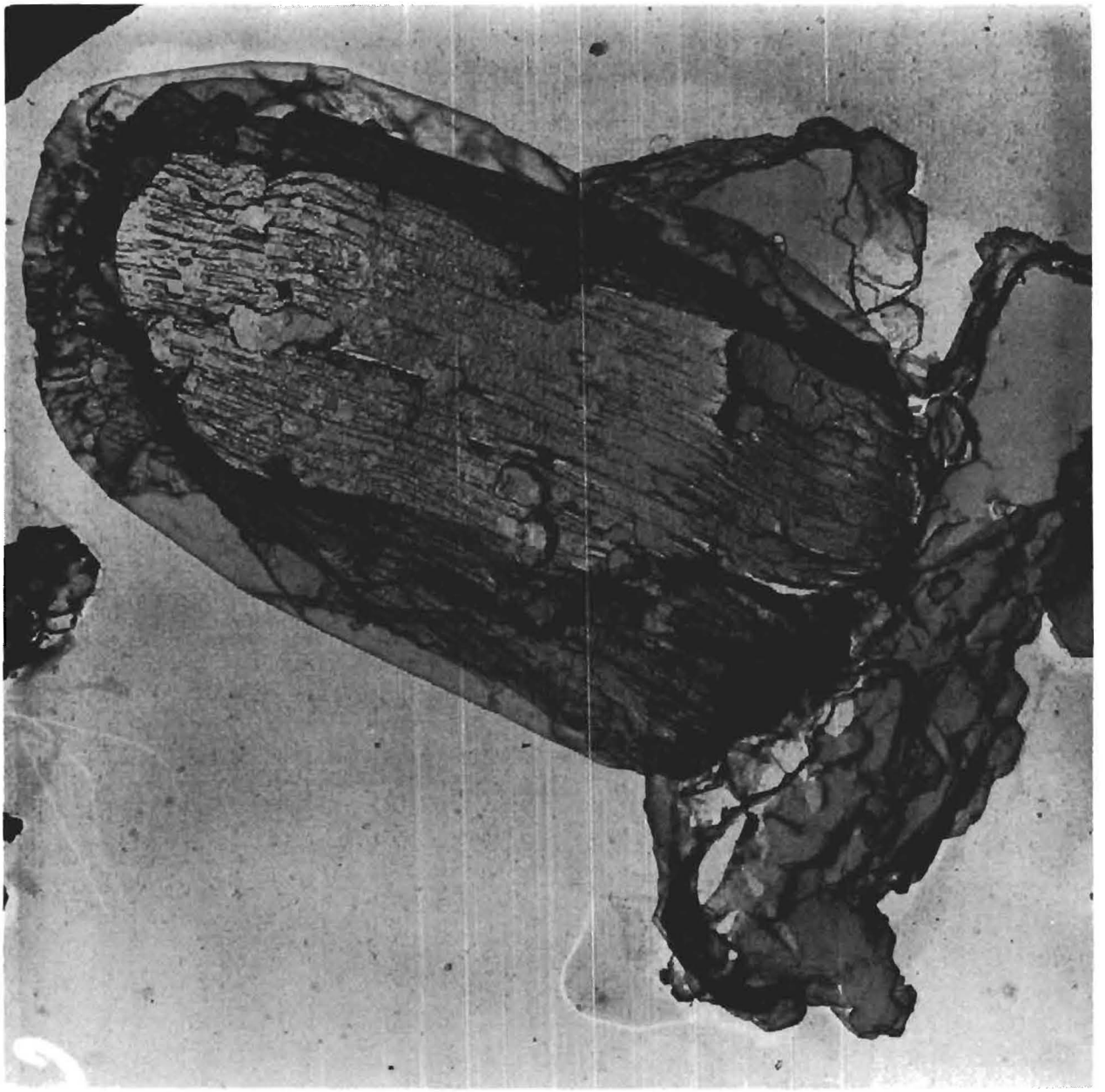


Figure 5. Electron Micrograph of Washington County Kaolin Exhibiting Surface Etching (13,400X).

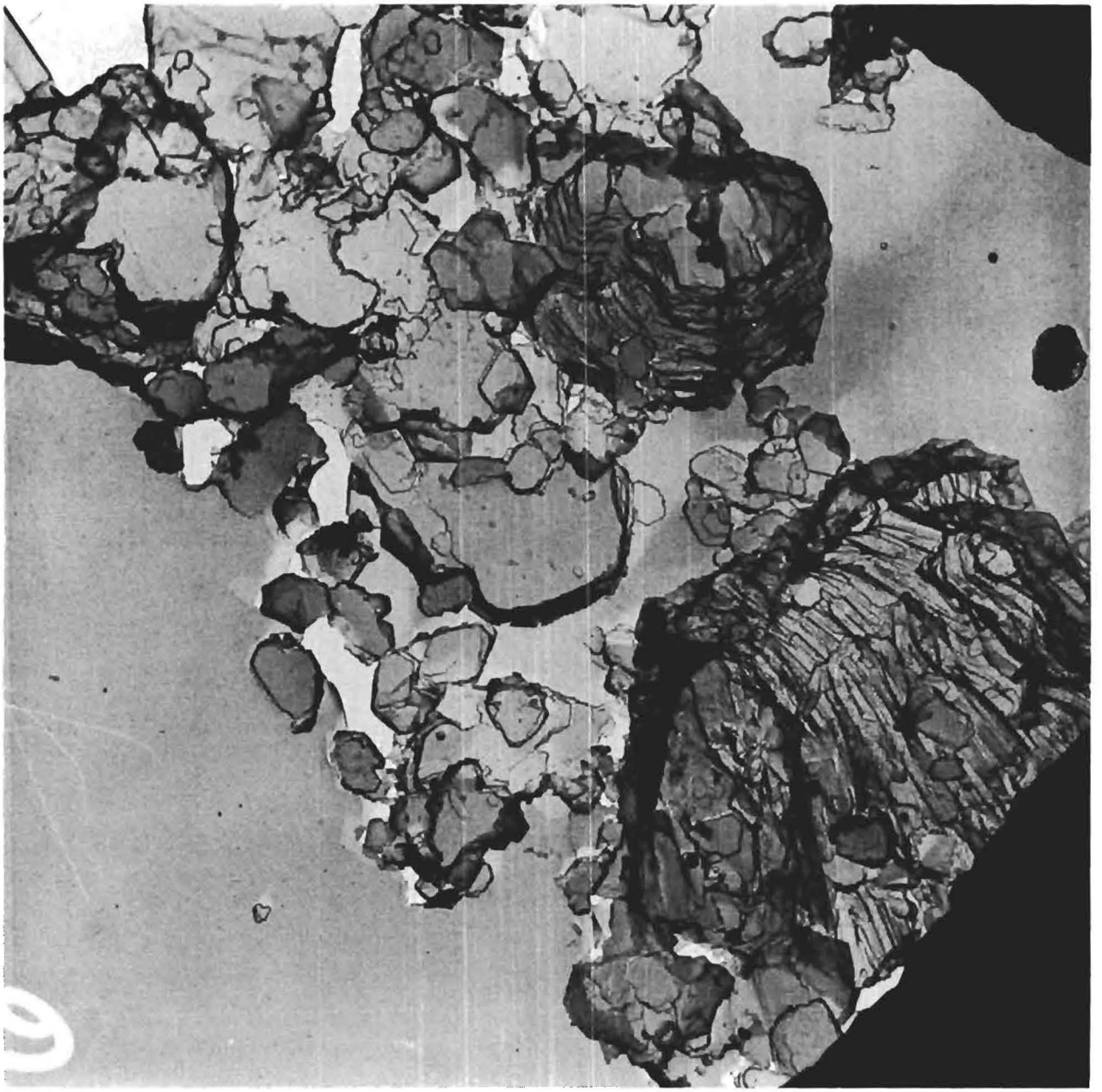


Figure 6. Electron Micrograph of Washington County Kaolin Exhibiting Surface Etching (13,400X).

the large stacks. A close examination of these micrographs reveals ridges and pits--some of which appear to be almost hemispherical--on the crystallite edges. Figures 7, 8, and 9 are micrographs of what appear to be kaolinite stacks with areas of vitrified material on their surfaces. The stack shown in Figure 9 contains areas suggestive of the early stages of mullite formation; a phase transition that normally occurs at about 960° C.

C. Particle Size Measurement

Size analysis methods have characteristically relied upon some measure of particle "diameter" as a criterion of particle size. Many methods have been developed and devised based on a variety of principles and depending upon different properties of the particle for their operation. Consequently, there is much confusion when one speaks of particle "diameters" as measured by different sizing methods. For instance, a "diameter" measured by a sedimentation technique depends upon the drag coefficient of the particle as it falls through a fluid; whereas the same "diameter," as measured microscopically, depends upon the judgment of the observer as to what its characteristic dimension is. The Coulter counter is one of a new series of "sensing zone" devices that have recently become available for particle size measurements. This device determines the number and size of particles suspended in an electrically conductive liquid. The suspension flows through a small aperture having an immersed electrode on either side, with a particle concentration such that the particles pass through the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperture, momentarily changing the resistance between the electrodes

Figure 7. Electron Micrograph of Washington County Kaolin Exhibiting Surface Etching and Vitrification (13,400X).

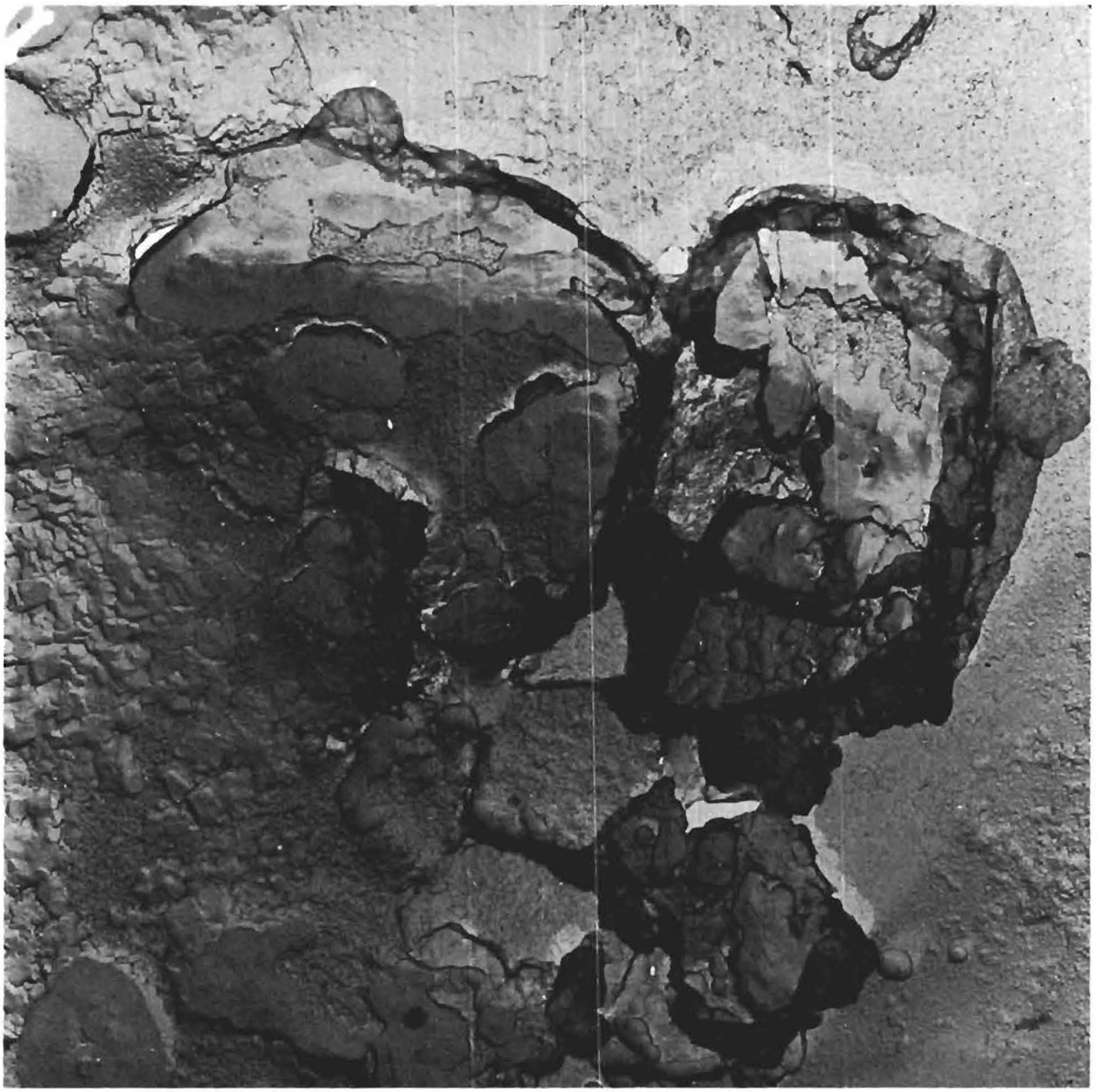


Figure 8. Electron Micrograph of Washington County Kaolin Exhibiting Surface Vitrification (13,400X).

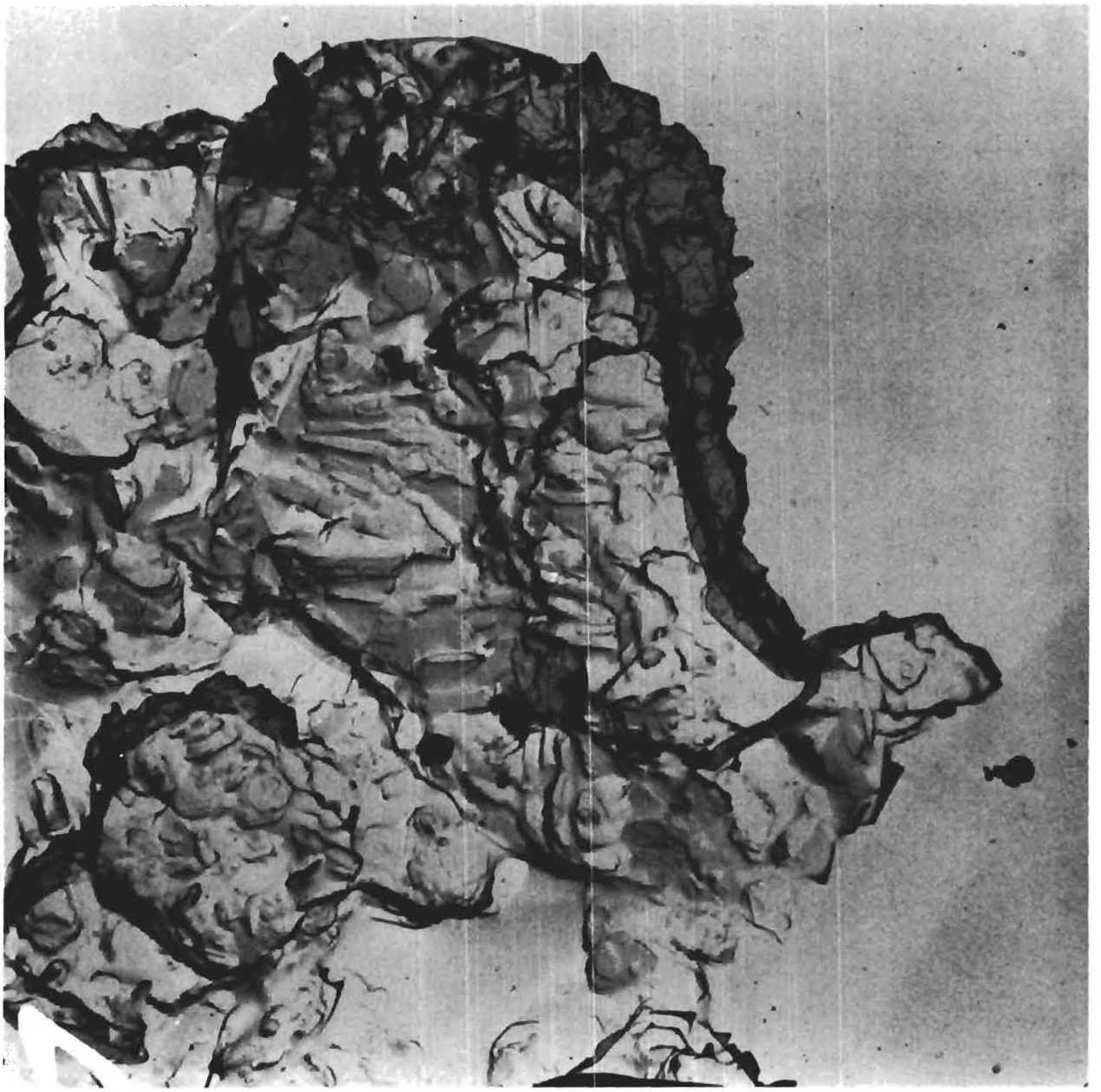


Figure 9. Electron Micrograph of Twiggs County Kaolin Exhibiting Surface Vitrification (13,400X).

and producing a voltage pulse of a magnitude proportional to particle volume. The resultant series of pulses is electronically amplified, scaled, and counted. This instrument measures, directly, the volume of a particle as it passes through an electric sensing zone. In the case of kaolin plates, which are flat and thin, a volume measure is much more meaningful than some fictitious diameter; therefore, the Coulter counter was selected as the best measuring device for this application.

The task of evaluating the effect of irradiation by particle-size-measuring techniques led to a number of difficult problems. During the first months of this project the lower limit of the Coulter counter was fixed at approximately 0.8-micron equivalent spherical diameter. However, a very few months before termination of the project the lower limit of the Coulter counter was lowered to approximately 0.2-micron equivalent spherical diameter by the production of smaller diameter aperture tubes. Two of the newer aperture tubes with orifice diameters of 20 and 10 microns were obtained on loan from Coulter Industrial Sales, Chicago, Illionis, and it was possible to investigate more completely the small end of the size distribution.

Attendant with the lowering of the limit of measurement of the Coulter counter, came the further problem of accurately measuring small particles in the presence of much larger particles. Large particles produce large voltage pulses in the amplifier portion of the instrument which tend to obscure the presence of very small particles. This ability of large particles to obscure changes in the smaller size ranges resulted in negligible observable differences in the respective overall size distributions of the two kaolins after exposure to high-energy radiation.

The small end of the overall size distribution was investigated by removing the large particles by a sedimentation technique. In this technique, a suspension of known concentration was prepared and allowed to settle for a sufficient length of time such that all particles larger than a given size had settled below a sampling point in the sedimentation tube. Fractionated samples of the Twiggs County kaolin, scaled to a common weight basis, exhibited a progressive increase in concentration of very small particles with increasing radiation dosage.

It was further observed during the analysis of the very small particles that there was a pronounced tendency for the particles to flocculate and cause a net change during the course of a size determination. This tendency indicated the presence of fewer small particles as time elapsed. This difficulty was alleviated by the use of tetrasodium pyrophosphate in the electrolyte medium to act as a suitable electrolyte for conduction of current between the electrodes of the Coulter counter and to provide a further synergistic benefit by being an effective dispersant for kaolin. An ultrasonic generator was used to assure proper initial dispersion of all samples whose size distributions were measured with the Coulter counter.

The overall size distributions of the two samples of kaolin used to date are presented in Figure 10. Figure 11 is a series of distributions of the smaller particles present in samples of kaolin from Twiggs County, Georgia, which had received varying doses of radiation. As can be seen from Figure 11, an increase of approximately 300 per cent was observed for the number of particles with volumes less than 10 cubic microns after a dose of 1×10^{22} electron-volts per gram of gamma-radiation. No reduction in particle-size was observed for the Washington County kaolin even after

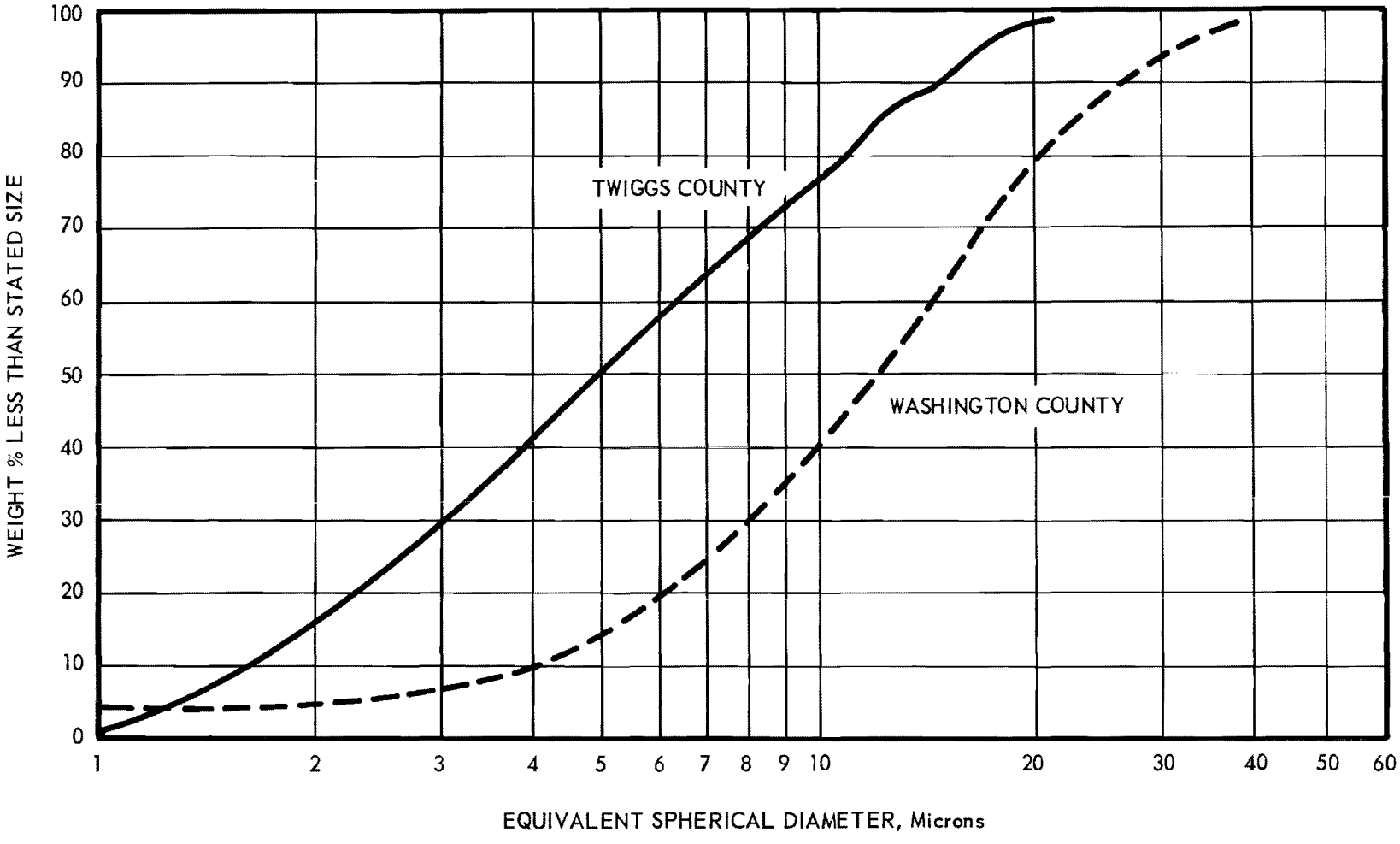


Figure 10. Particle Size Distributions of the Washington County Twiggs County Kaolins.

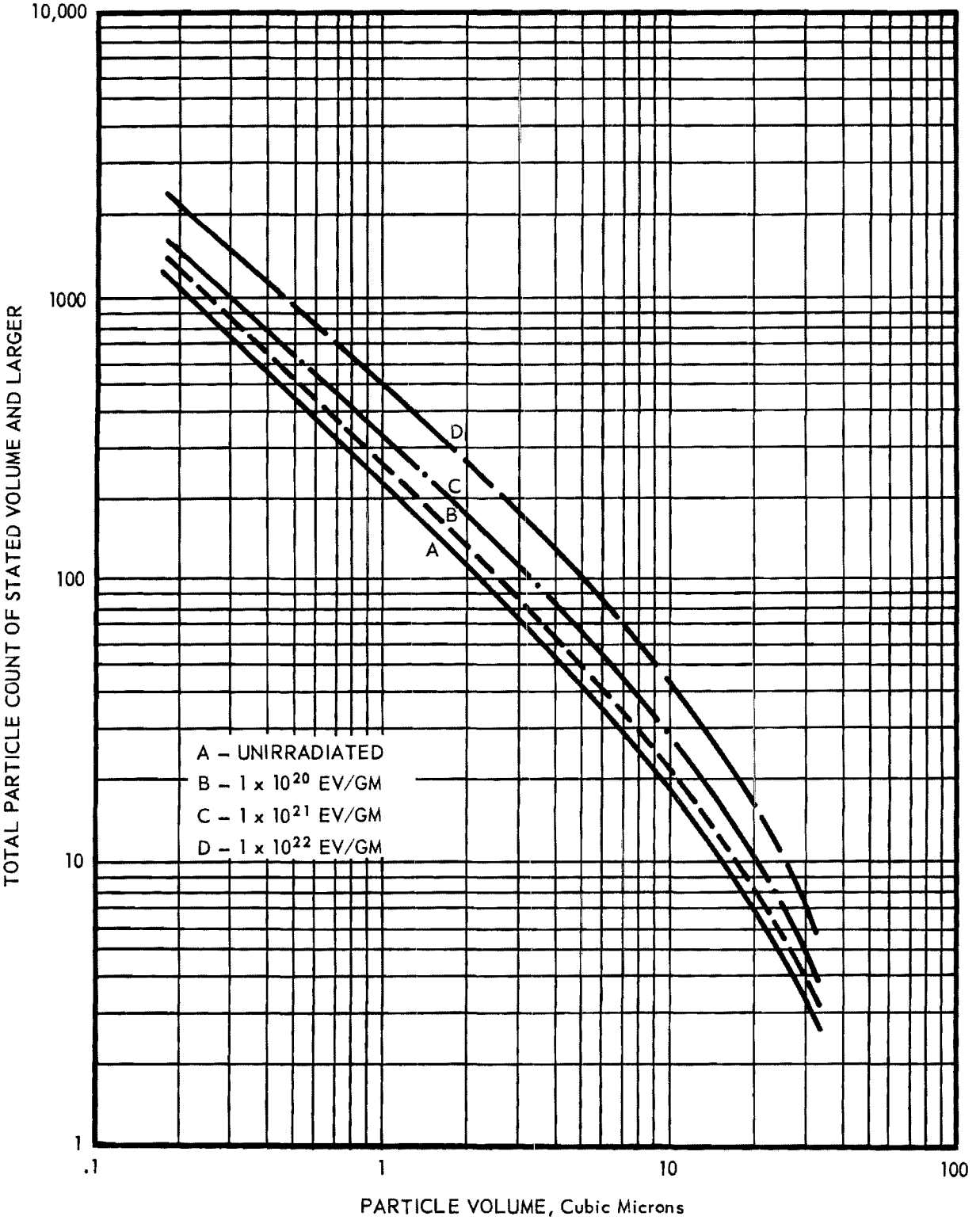


Figure 11. Distribution of Particles with Volumes of $10\mu^3$ or Less for Samples of Twiggs County Kaolin Before and After Irradiation.

1×10^{22} electron-volts per gram of gamma-radiation, and fractionation to isolate the smaller particles.

D. Surface Area Measurements

Specific surface areas were measured for samples of both kaolins used in these studies as a function of radiation dose. The Brunauer, Emmett and Teller[7] method of low-temperature, nitrogen-gas adsorption was used in the determinations. The cross-sectional area of the nitrogen molecule was taken as 15.8 square angstroms.[8] These results are presented in Table I.

TABLE I

SPECIFIC SURFACE AREA OF KAOLIN AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area: Washington County Kaolin (M^2/Gm)	Specific Surface Area: Twiggs County Kaolin (M^2/Gm)
Unirradiated	6.1	7.2
1×10^{18}	5.4	6.7
5×10^{18}	5.4	6.6
1×10^{19}	4.7	6.0
5×10^{19}	5.0	6.7
1×10^{20}	5.0	6.0
1×10^{21}	4.5	6.1
1×10^{22}	4.5	5.5

[7] S. Brunauer, P. H. Emmett, and E. Teller, "The Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc. 60, 209-19 (1938).

[8] A. S. Joy, "The Determination of Specific Surface by Gas Adsorption," Vacuum 3, 254-78 (1953).

The data contained in Table I have been plotted in Figure 12 to illustrate the trend of specific surface area with increasing radiation dose.

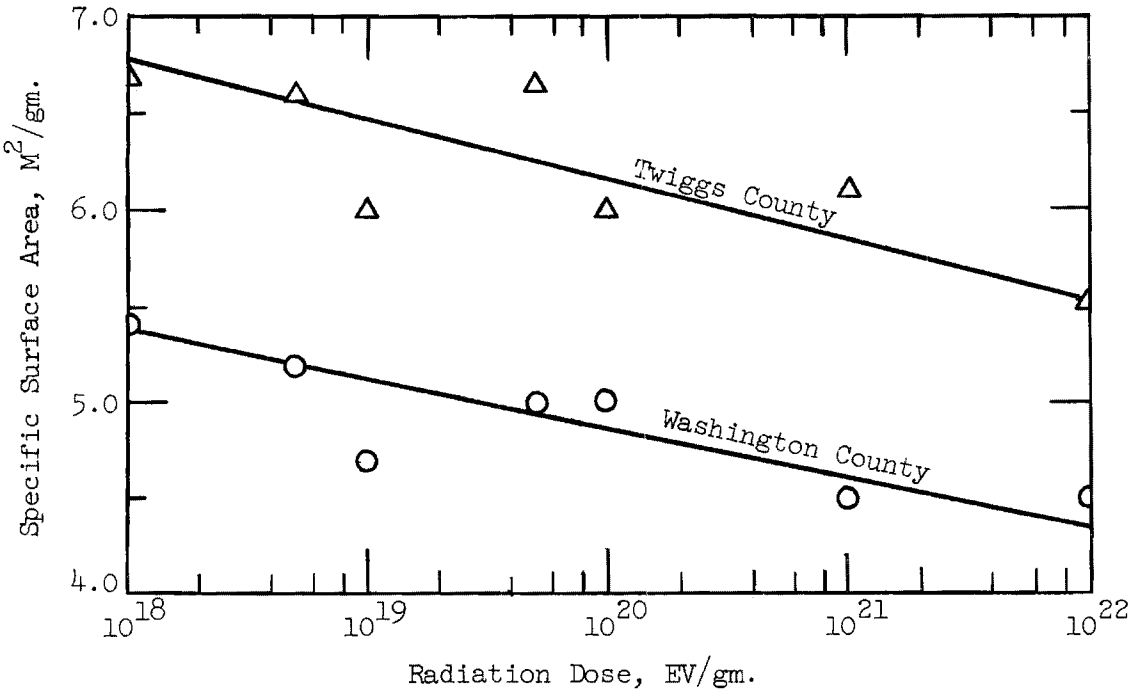


Figure 12. Specific Surface Area of Kaolin as a Function of Radiation Dose.

The trend is unquestionably a decreasing one in spite of the observed scatter in the data. A decrease of approximately 25 per cent between the unirradiated material and the samples that had received 1×10^{22} electron-volts per gram was found for both kaolins. From repeated measurements on several samples the reproducibility of the specific surface area measurements was found to be ± 3 per cent. Since the specific surface area of the kaolins decreased with increasing radiation dose, complete adsorption isotherms were obtained for several samples to determine

if the number of pores and capillary cracks were changing also. When a significant number of cracks and crevices are present, as they undoubtedly are in the kaolin stacks, the surface area of the material will appear to be larger than it actually is. Multilayer adsorption takes place in these capillaries while monolayer adsorption is taking place on the surface, and when the surface area is evaluated on the basis of monolayer adsorption, the capillaries make a disproportionate contribution. If these sites for capillary condensation are then destroyed and the surface area redetermined, a lower value will be obtained for the specific surface area. The difference in the number of cracks and crevices for two samples can be evaluated by determining total adsorption isotherms for the samples. If adsorption is taking place in a limited space such as a capillary crack rather than a free surface, only a finite number of layers can be adsorbed at saturation. The results of these measurements, however, were inconclusive. The deviations in experimental results were of the same order of magnitude as any differences that were observed. This technique is actually better suited to highly porous materials such as porous silicas and carbon blacks. Very careful determinations of pore volume by the adsorption and subsequent desorption of nitrogen could possibly measure any change in the number or size of the capillary cracks, but time limitations would not permit measurements of this type.

E. Crystallinity Studies

All samples of both the Washington County and Twiggs County kaolin that had been subjected to gamma-radiation were examined by X-ray diffraction. These studies were made to determine what structural disorder had been produced in the kaolinite by the gamma-radiation. The customary

method of evaluating differences in the degree of crystal perfection of kaolinite is to make qualitative rankings by inspection of diffractometer traces; the bases for rankings being loss of resolution for certain diffraction maxima and the absence of certain diffraction maxima. From this qualitative point of view, the samples of kaolin that had been irradiated were less well crystallized than the unirradiated kaolin. Two typical X-ray diffractometer traces are presented in Figure 13 for a sample of unirradiated kaolin and a sample that had received 1.0×10^{22} electron-volts per gram of gamma-radiation. From these traces the loss of resolution of such diffraction maxima as the (020), ($1\bar{1}0$) and ($11\bar{1}$)(areas enclosed by the dotted lines) can readily be seen; the intensities and relative intensities of the (001) and (002) maxima are changed; and such maxima as the (111), (004), (203), and three minor maxima beyond (060) have disappeared almost completely for the irradiated material. These particular traces were made with CuK_{α} radiation, at one degree (2θ) per minute, a chart speed of 15 inches per hour, a time constant of 4 seconds, a scale factor of 8, at 40 kv and 20 ma using a slit width of 6 mils with a Geiger counter.

The above method of qualitative rankings was not adequate for establishing degree of change in crystallinity as a function of radiation dose. Therefore, the recently developed method of Johns and Murray[9] was used to obtain an empirical "index of crystallinity." This method employs a ratio of the intensities of two reflections, one which is affected by $nb_o/3$ translations of kaolinite layers (021), and one which

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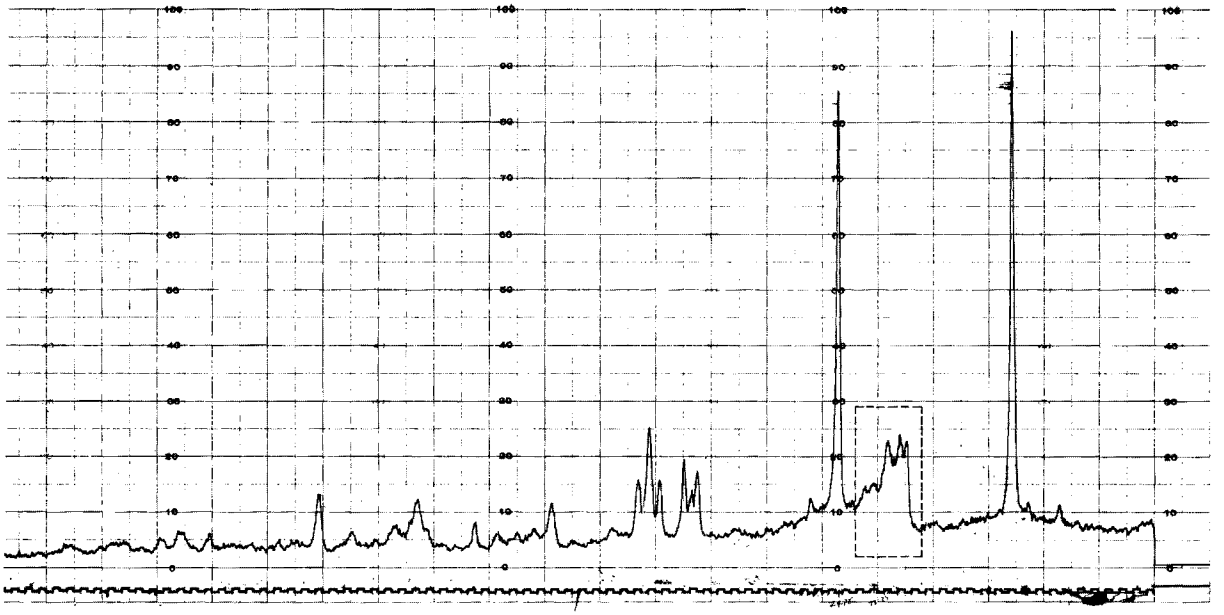
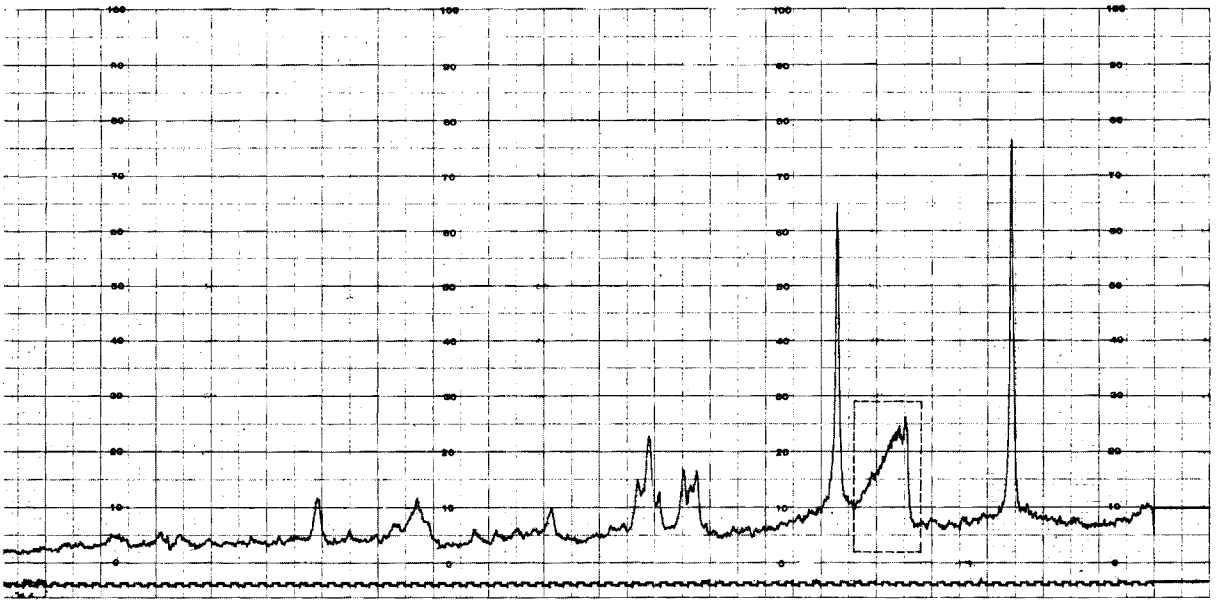
[9] W. D. Johns and H. H. Murray, "An Empirical Index for Kaolinite Crystallinity," Paper presented at the 1959 meeting of the Mineralogical Society of America. To be published in Am. Mineral.



A. UNIRRADIATED KAOLIN



B. IRRADIATED KAOLIN
1×10^{22} EV/GM

Figure 13. Typical X-Ray Diffractometer Traces for Washington County Kaolin.

is not (060). For this reason a more descriptive term for this ratio would seem to be an "index of $nb_o/3$ crystallinity." The ratio has been found to vary from 0 to approximately 1, with 1 being the best crystallized material and 0 the poorest. The first attempts at obtaining traces of these maxima met with very limited success. The Washington County kaolin had a relatively low crystallinity and a large particle size that promoted some sample orientation. As a result, the $(02\bar{1})$ maximum had a very low intensity and a very strong CuK_β reflection from the (002) crystallographic plane appeared very near the $(02\bar{1})$ maximum. After trying a number of techniques, this difficulty was finally overcome by the use of a high intensity X-ray tube. This tube, operated at 40 kv and 40 ma, produced reflections of sufficient intensity that a beta filter could be used to significantly reduce the intensity of the CuK_β reflection. The use of a proportional counter and a pulse height analyzer in conjunction with the beta filler permitted very good resolution of the $(02\bar{1})$ maximum. The samples of Twiggs County kaolin, while not subject to these difficulties, were also analyzed with this same arrangement.

The integrated intensity of the (060) reflection could be readily evaluated since no other reflections are located immediately adjacent to it. This, however, was not the case for the $(02\bar{1})$ reflection since portions of this reflection probably overlap into the region in which the (002) reflection occurs on one side and into the region in which the beta-reflection of the (002) reflection occurs on the other side. Therefore, only the area over a fixed angular region was measured (2θ equal to 22.75° - 23.50°), and the relative change in this area taken as being proportional

to the change in the total area. The crystallinity indices calculated from these data are presented in Figures 14 and 15. The indices of $nb_o/3$ crystallinity are primarily a measure of the amount of disorder produced in the arrangement of aluminum atoms in successive layers ($nb_o/3$ translations). The significance of the maxima observed in the curves of Figures 14 and 15 is not readily apparent. Strictly in terms of the index of $nb_o/3$ crystallinity as devised, these maxima imply that the arrangement of aluminum atoms in the kaolinite lattice becomes more ordered with radiation up to a dose of about 5×10^{18} and then becomes progressively less ordered with increasing radiation dose. However, from the standpoint of what is known concerning radiation-damage processes in general, and an intuitive feeling for the entropy changes demanded by such an event, the possibility of a more orderly arrangement of the aluminum atom seems most unlikely. One factor which must be considered is that not only was the intensity of the $(02\bar{1})$ reflection changing, but the intensity of the (060) was also changing. That is to say, not only were the aluminum atoms being displaced, giving rise to apparent $nb_o/3$ translations, but disorder was also being produced in the remainder of the lattice by displacements of other atoms. Since nothing is known concerning the rates of displacement production or the recombination rates, except that the intensity of the $(02\bar{1})$ reflection underwent a much greater reduction with increased radiation dose than did the intensity of the (060) reflection, it can be seen that any firm interpretation of a maximum in the ratios is impossible at the present time. The fact that an overall decrease in the index of $nb_o/3$ crystallinity with radiation dose was observed, coupled with the fact that the $(02\bar{1})$ maximum always exhibited an intensity decrease as the

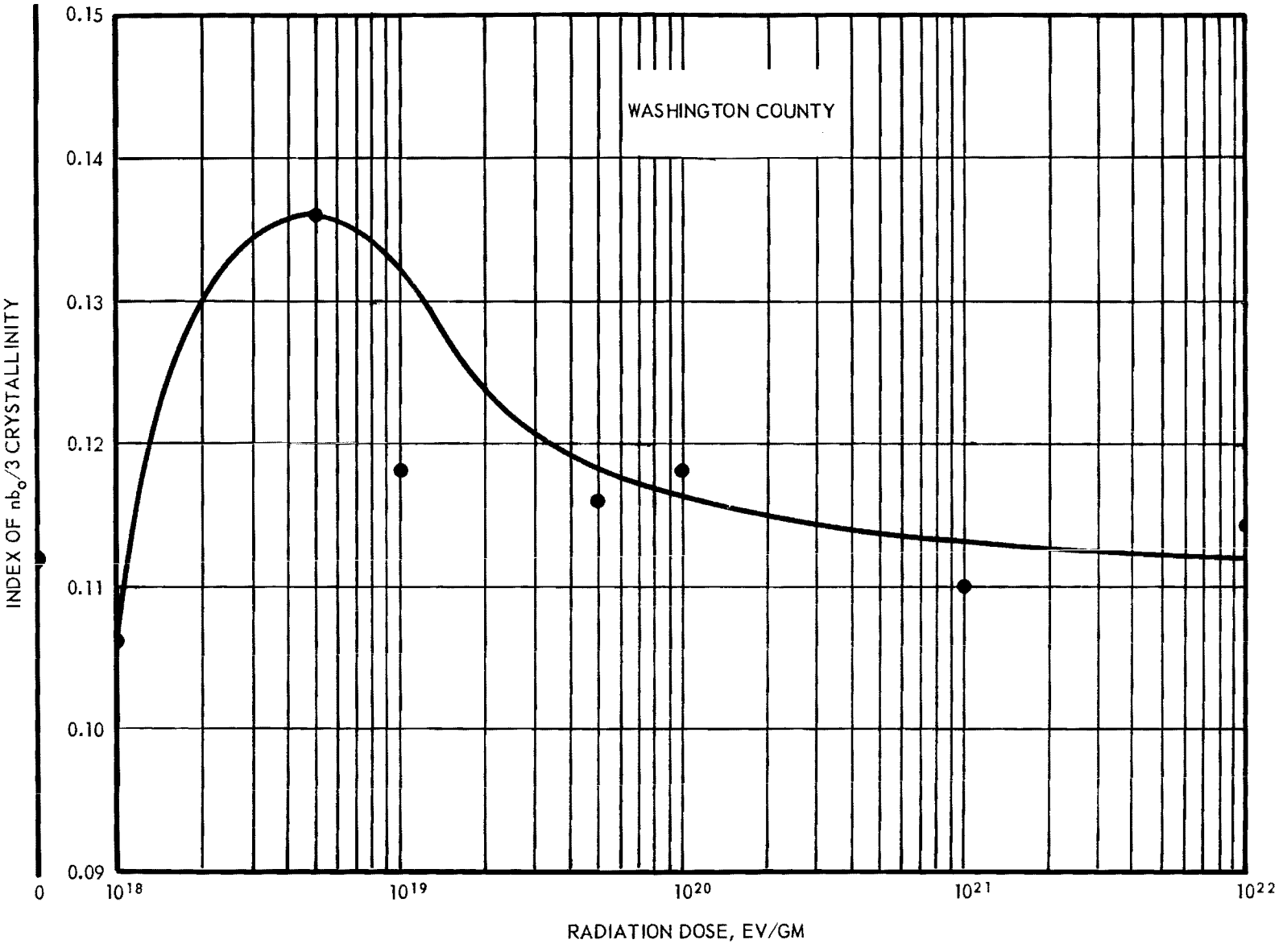


Figure 14. Index of $nb_o/3$ Crystallinity as a Function of Radiation Dose for Washington County Kaolin.

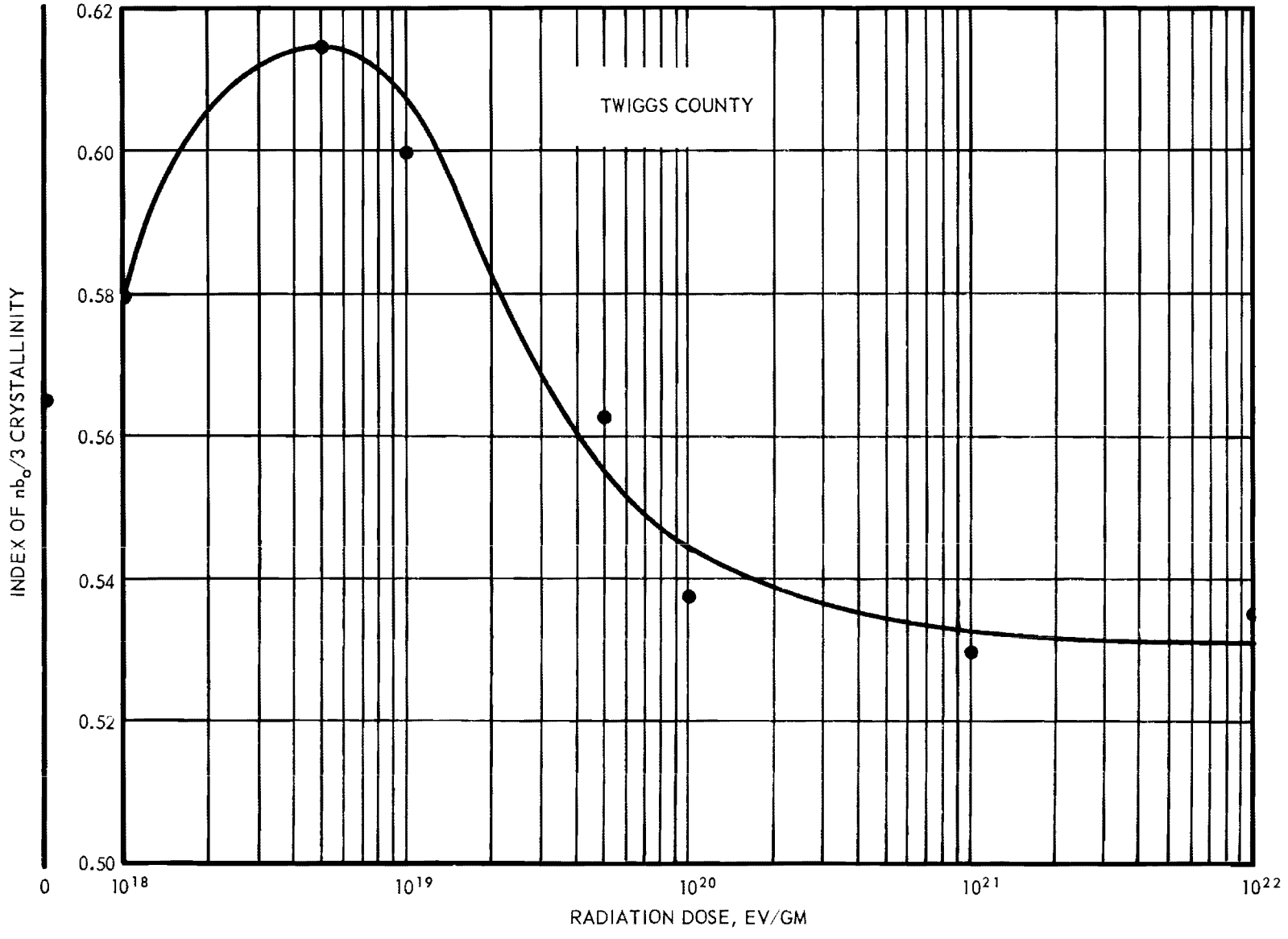


Figure 15. Index of $nb_o/3$ Crystallinity as a Function of Radiation Dose for Twiggs County Kaolin.

radiation dose was increased, does, however, indicate that disordering of the aluminum atom was obtained.

In a radiation-damaged material, localized, static, lattice defects are produced which are usually considered to be isolated interstitial lattice atoms, vacancies, and perhaps rather small agglomerates of these defects. If a sufficiently large number of these defects are built up, they can be detected by X-ray diffraction. Zachriasen,[10] Huang,[11] and Borie[12] have been significant contributors to a general theory of the X-ray effects to be expected from localized static lattice defects in crystals. These treatments postulate that displacement of atoms from their normal lattice sites leads to a reduction in the integrated intensities of Bragg maxima by a factor $\exp[-2M']$ and to diffuse scattering. It can be shown in a manner exactly analogous to that for the well known temperature factor of X-ray scattering for crystals that

$$\exp[-2M'] = \exp[16\pi^2 \ \bar{u}_d^2 \ \mathrm{Sin}^2 \theta/\lambda^2] \qquad (1)$$

where $\bar{u}_d^2$ is the mean square of the average atomic displacement in one dimension, θ is the Bragg angle, and λ is the wave length of the X-radiation. Therefore, the ratio of the peak area of a radiation-damaged sample to peak area of an undamaged sample for the same reflection should give

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[10] W. H. Zachriasen, Theory of X-Ray Diffraction in Crystals, (New York: John Wiley and Sons, 1947).

[11] K. Huang, "X-Ray Reflections from Dilute Solutions," Proc. Royal Soc. London A 190, 102-17 (1947).

[12] B. Borie, "X-Ray Diffraction Effects of Atomic Size in Alloys," Acta. Cryst. 10, 89-96 (1957).

$$I_o/I_d = \exp\left[(-2\Delta M) - 16\pi^2 \bar{u}_d^2 \Delta(\mathrm{Sin}^2 \theta/\lambda^2)\right] \qquad (2)$$

where the term $(-2\Delta M)$ represents the difference in the Debye factors for ordered and disordered samples. This particular analysis, however, requires the use of absolute intensities. A more convenient analysis is to compare the ratios of intensities for different orders of the same reflection for the undamaged material and the irradiated material. The integrated intensities of different orders of the same reflection are reduced in the same manner as outlined in the above analysis

$$\left[\frac{I_{hkl}}{I_{n(hkl)}}\right]_d = \left[\frac{I_{hkl}}{I_{n(hkl)}}\right]_o \cdot \exp\left[-16\pi^2 \bar{u}_d^2 \Delta(\mathrm{Sin}\,\theta/\lambda^2)\right] \qquad (3)$$

where the subscripts d and o refer to the irradiated and unirradiated material respectively, and n is some integer.

Equation 3 was used with the integrated intensities of the (001) and (002) reflections from the X-ray diffraction traces to obtain a root mean square of the average atomic displacement along the c axis for the samples of irradiated kaolin. These data are presented in Figure 16. Since the root mean square of the average atomic displacement is dependent upon the number of displacements, these values are a measure of the number of defects present in the lattice as a function of the absorbed radiation-dose. In this analysis the difference in the Debye factors was assumed negligible. This is not exactly true since the elastic constants were no doubt altered by the radiation damage. However, this should amount to only a very few per cent at most. It should be noted that the above theory predicts that there should be no broadening of the

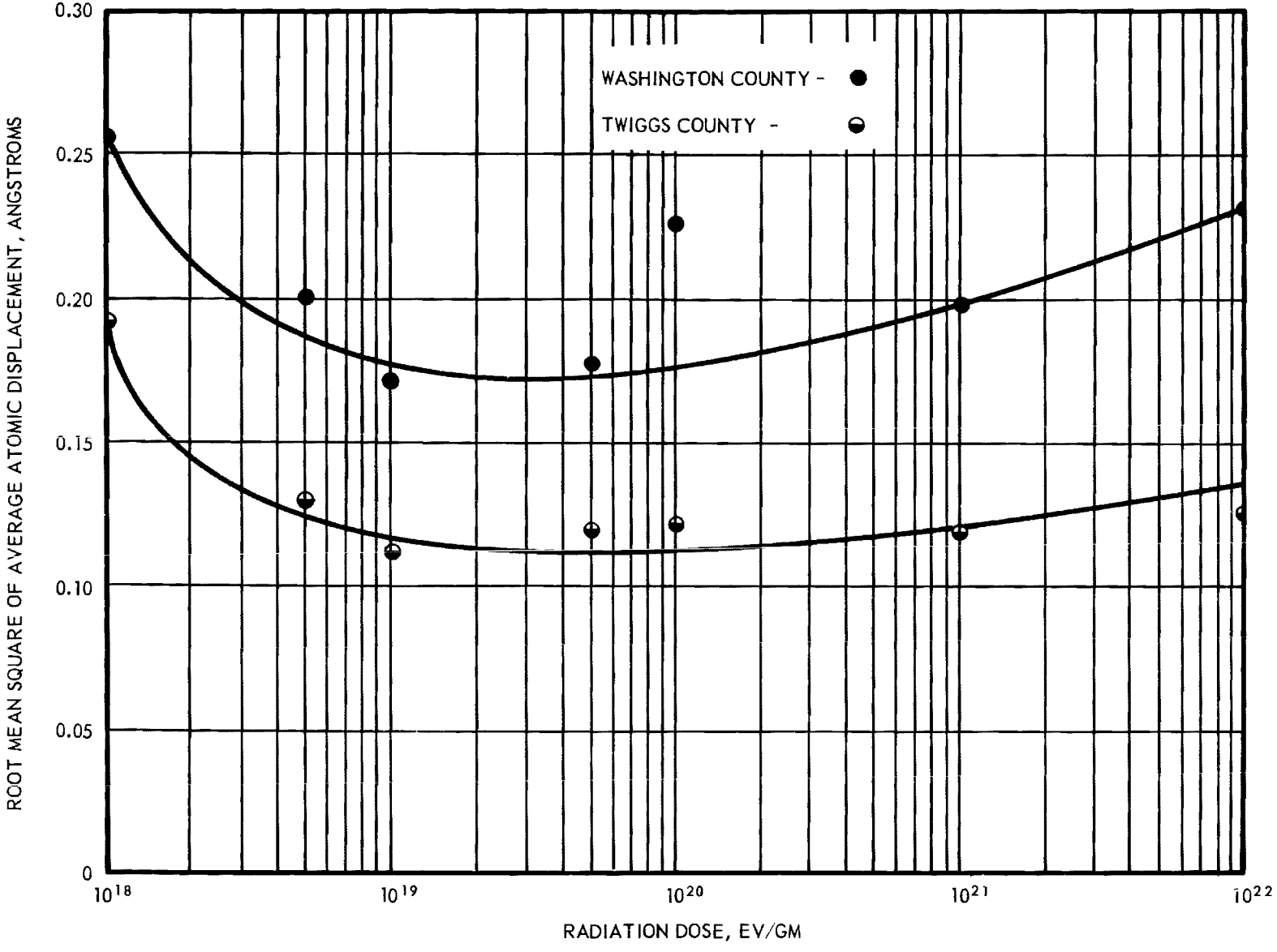

Figure 16. Root Mean Square of the Average Atomic Displacement as a Function of Radiation Dose.

diffraction peaks, and none was observed.

F. Differential Thermal Analysis

Irradiated and unirradiated samples of both the Washington County and Twiggs County kaolin were subjected to differential thermal analysis. This technique involves comparison of the changes that occur in a clay sample with those of a reference material, as a function of temperature. A few grams (2 or 3) of the kaolin being tested are compressed into a pellet. This pellet, along with a pellet of the reference material, is heated at a constant rate in a suitable furnace to some arbitrary temperature, and the difference in temperature between the two pellets is recorded. The temperature differences observed are indications of endothermic and exothermic processes that are taking place in the kaolin. The magnitude of these differences and the range at which they occur are determined by the chemical composition and the physical condition of the kaolin. The reference material is usually calcined alumina. However, in this work a calcined pellet of the unirradiated kaolin was used as the standard. Figure 17 shows a typical plot of the data obtained from a differential thermal analysis. The abscissa is the temperature to which the pellets have been heated, with 1000° C being the maximum for this work, and the ordinate is the millivolt difference between the Pt - Pt10Rh thermocouples placed beneath each pellet. The first deviation along the abscissa, which is negative--indicating an endothermic process, extending from a temperature of approximately 60° C to a temperature of approximately 375° C--is caused by the driving off of absorbed water. The next deviation, also an endothermic process, extending from a temperature of about 475° to 850° C, is the result of driving off chemically bound water from the

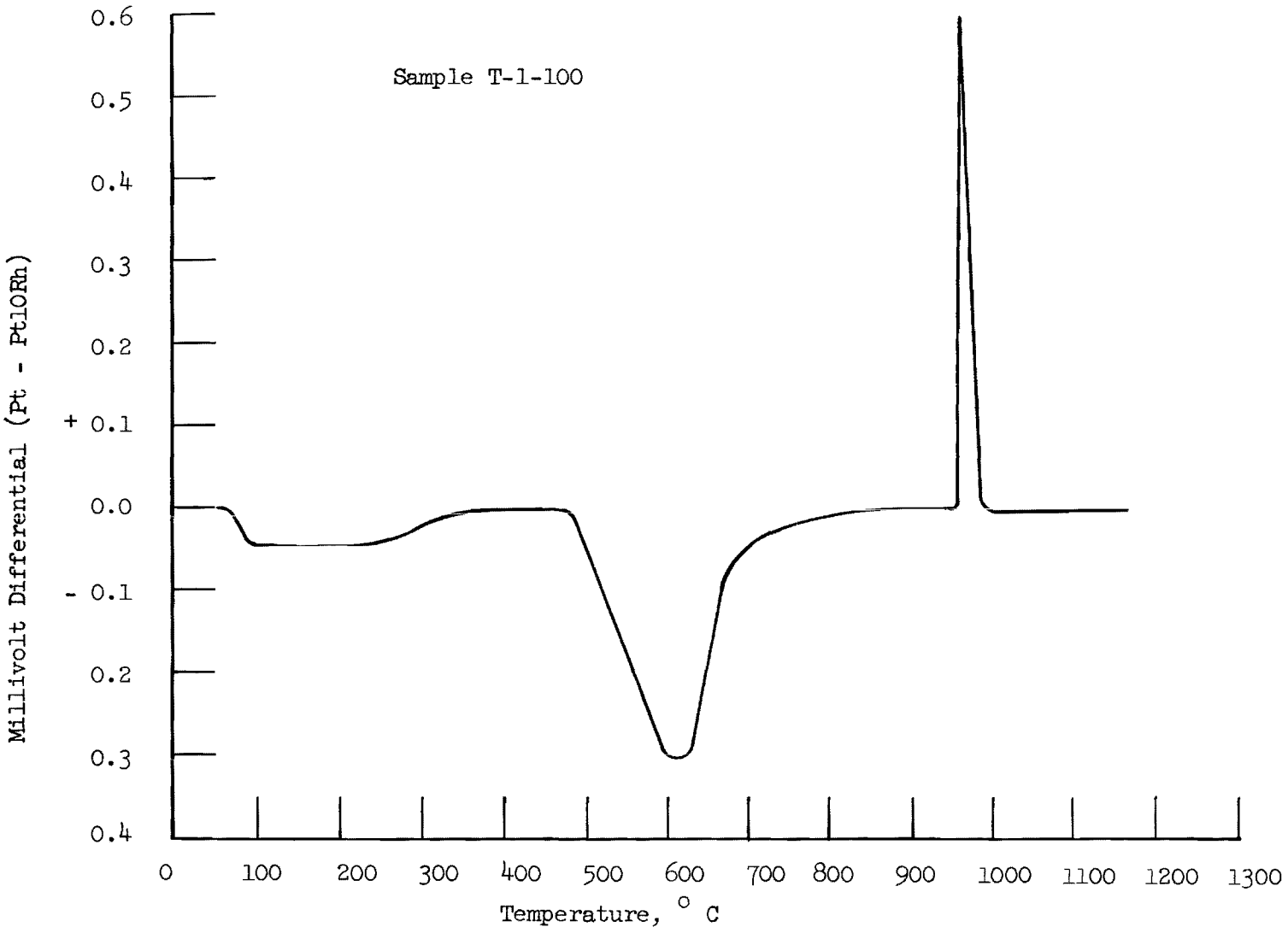

Figure 17. Typical Plot of Differential Thermal Analysis Data.

crystal lattice. This process, which is actually calcination of the kaolin, has a maximum at 625° C. The final deviation, which is an exothermic process, is the result of a phase change that takes place at about 965° C. These analyses were performed in an attempt to measure the amount of stored energy due to dislocations in the crystal lattices, and as a corollary method of determining the amount of structural disorder. No difference was found between the data obtained from the irradiated kaolin and that obtained with unirradiated kaolin. This was probably due to the fact that the apparatus used was not sensitive enough to detect the difference in the temperature of the exothermic phase transition which should have resulted from the crystalline disorder detected in the X-ray diffraction work. Also, the integrated area of the exothermic phase transition peak should have varied with radiation dose due to the extra energy stored in the lattice by the atomic displacements. However, when these analyses were performed, the fact that this effect should have been present was not recognized, and no particular attempt was made to keep the upper portion of this peak on the recorder scale. Unfortunately, time limitations would not permit these analyses to be repeated. Other investigators have shown, however, that the temperature at which this transition phase occurs is altered by the effects of gamma-radiation on kaolinite.[13]

G. Infrared Absorption Measurements

The infrared absorption spectra for samples of the Washington County kaolin that had received various doses of gamma-radiation were carefully examined for any changes in hydroxyl absorption. In these studies

[13] C. A. Head, "Effect of Radiation on Formation of Mullite in Kaolinite," Masters Thesis, School of Ceramic Engineering, Georgia Institute of Technology (1961).

0.5-inch-diameter wafers or potassium bromide containing 1.0 per cent by weight of kaolin were prepared by pressing 0.01 gram of the mixture at 12.5 tons per square inch in an appropriate press. These wafers were examined with a Perkin-Elmer Model 21 spectrophotometer, Perkin-Elmer Corporation, Norwalk, Connecticut, using a rock salt optical system. The unbonded OH in kaolinite produces a strong absorption maximum at 2.70 microns. Other OH absorption maxima appearing in the kaolinite spectrum are: at 2.75 microns, a moderate shoulder from 2.87 to 2.92 microns, and a fairly strong maximum at 6.15 microns.[14,15,16] The adsorption maximum at 2.75 microns is apparently associated with long hydrogen bonds. The absorption maximum at 6.15 microns appears to be a result of water adsorbed on the surface of the kaolin. Although this maximum is always found in the spectrum when the kaolin samples are handled in a normal manner, it is not observed when rigorous techniques are employed for drying and excluding the readsorption of water. The shoulder observed from 2.87 to 2.92 microns appears also to be associated with adsorbed water. As semi-quantitative measures of the relative amounts of bonded and unbonded hydroxyl groups associated with the kaolinite, a ratio, R_1, of the relative intensities of the maximum at 2.70 microns to the maximum at 2.75 microns and a ratio, R_2, of the relative intensitites of the maximum at 2.70 microns to the maximum at 6.15 microns to the maximum at 6.15 microns, were calculated. The ratio, R_1,

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[14] J. M. Hunt, M. P. Wishero, and L. C. Bonham, "Infrared Absorption Spectra of Minerals and Other Inorganic Compounds," Analytical Chemistry 22, 1478-97 (1950).

[15] J. P. Lyon and W. M. Tuddenham, "Infrared Determination of the Kaolin Group Minerals," Nature 185, 835-36 (1960).

[16] W. D. Keller and E. E. Pickett, "The Adsorption of Infra-red Radiation by Clay Minerals," Amer. J. Sci. 248, 264-73 (1950).

is therefore a measure of the relative amounts of unbonded OH groups in the kaolinite to the bonded OH groups. The ratio R_2 is a measure of the relative amounts of adsorbed water on the kaolinite. The fact that the intensity of the absorption maximum at 6.15 microns (apparently representing adsorbed water) was referred to the intensity of the absorption maximum at 2.70 microns has no significance other than serving to eliminate any effect of concentration differences between pellets. The values obtained for R_1 and R_2 are presented in Table II. The ratio R_1 shows a slight increase with irradiation dose indicating the possibility of an increase of the amounts of unbonded to bonded OH groups in the kaolinite. However, the change is relatively small and may not be significant. This could be established only with further investigation with a complete error analysis. The ratio R_2 shows a very significant increase with irradiation dose that strongly indicates exposure to gamma-radiation decreases the affinity of the kaolinite for adsorbing water vapor. A significant change was noted for the shoulder of the adsorption spectra extending from 2.82 to 2.92 microns. The width of this shoulder decreased significantly with increasing radiation dose, disappearing almost entirely for the higher radiation doses.

TABLE II

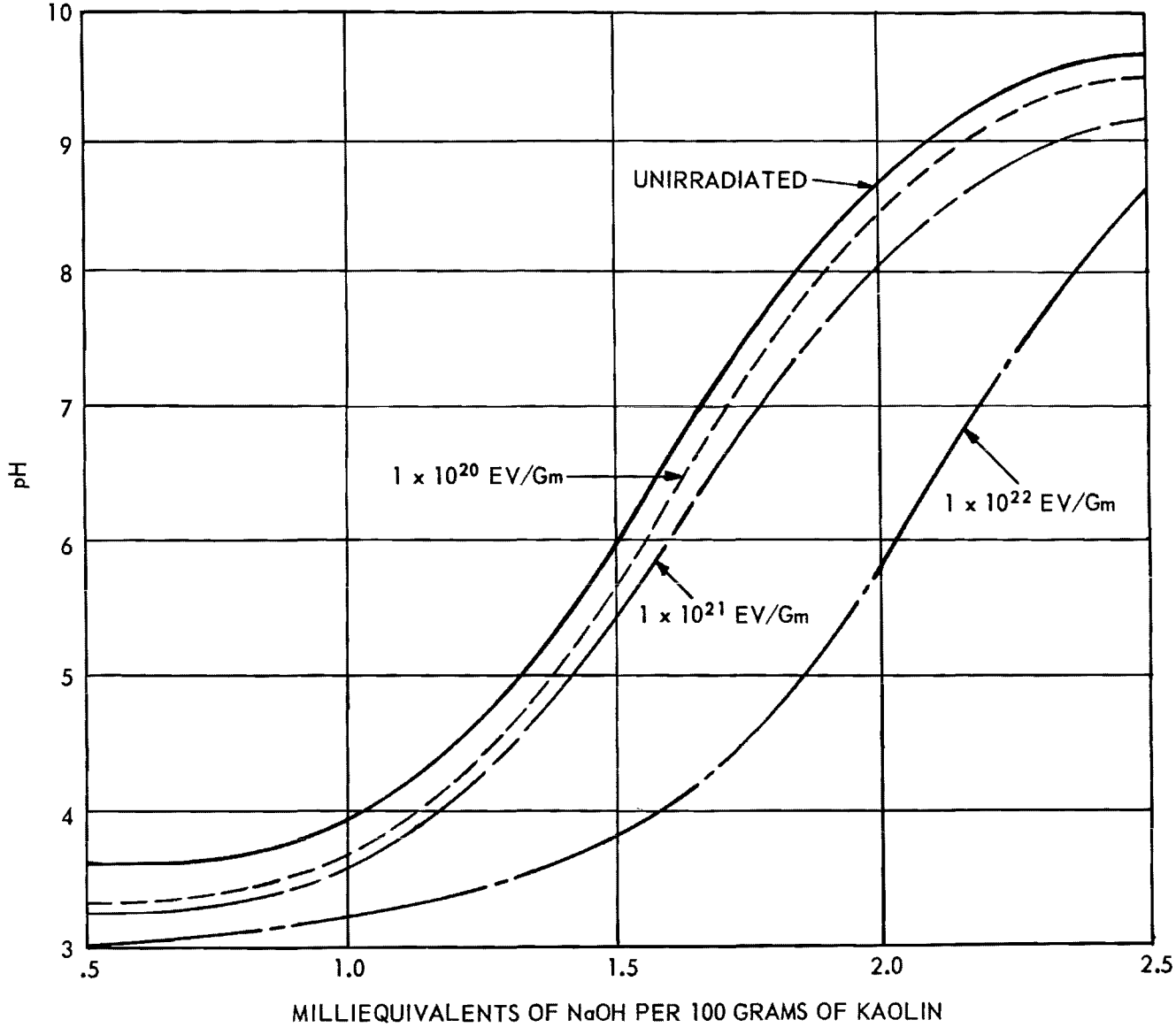
VARIATION OF RATIOS OF OH ABSORPTION INTENSITIES WITH RADIATION DOSE FOR WASHINGTON COUNTY KAOLIN

Dose	R_1	R_2
Unirradiated	1.150	6.3
1.0×10^{20}	1.177	9.2
1.0×10^{21}	1.18_2	8.9
1.0×10^{22}	1.18_2	11.4

H. Cation-Exchange Measurements

The cation-exchange capacities of the clays used in these studies have been measured as a function of radiation dose. This measurement, while not difficult in technique is quite sensitive, and particular care must be exercised to insure that the various samples for a series of determinations receive identical treatment. Five-gram quantities of each sample from a series of irradiations of kaolin were dried simultaneously for 3 hours in an oven at 110° C, treated with 50 ml of dilute hydrochloric acid for 2 hours, and then filtered and washed with distilled water. These "acid" clays were then dried to constant weight in an oven at 110° C, and a 20-percent-by-weight suspension in distilled water was prepared. These clay suspensions were then titrated with a 0.1023N sodium hydroxide solution, with pH determinations after the addition of each 0.1 ml of sodium hydroxide until a pH of 7.0 was reached. The pH determinations was made with a Beckman Model 96 Zeromatic pH meter, Beckman Instruments, Inc., Fullerton, California. These data are presented in Figures 18 and 19.

The behavior of these kaolins appears to be completely anomalous. The cation-exchange capacity of the Washington County kaolin increases with increasing radiation dose while that of the Twiggs County kaolin decreases. However, an explanation may lie in the treatment the two kaolins received before irradiation. The Washington County kaolin was fractionated according to particle size and had been treated with a deflocculating agent such as tetrasodium pyrophosphate. Some cation-exchange with sodium no doubt occurred at this time. This view is supported by the fact that the cation-exchange capacities of the two kaolins before irradiation were almost identical while the X-ray diffraction results showed a significant difference in the crystallinity



18. Titration Curves for Hydrogen-Kaolinite Prepared from Washington County Kaolin.

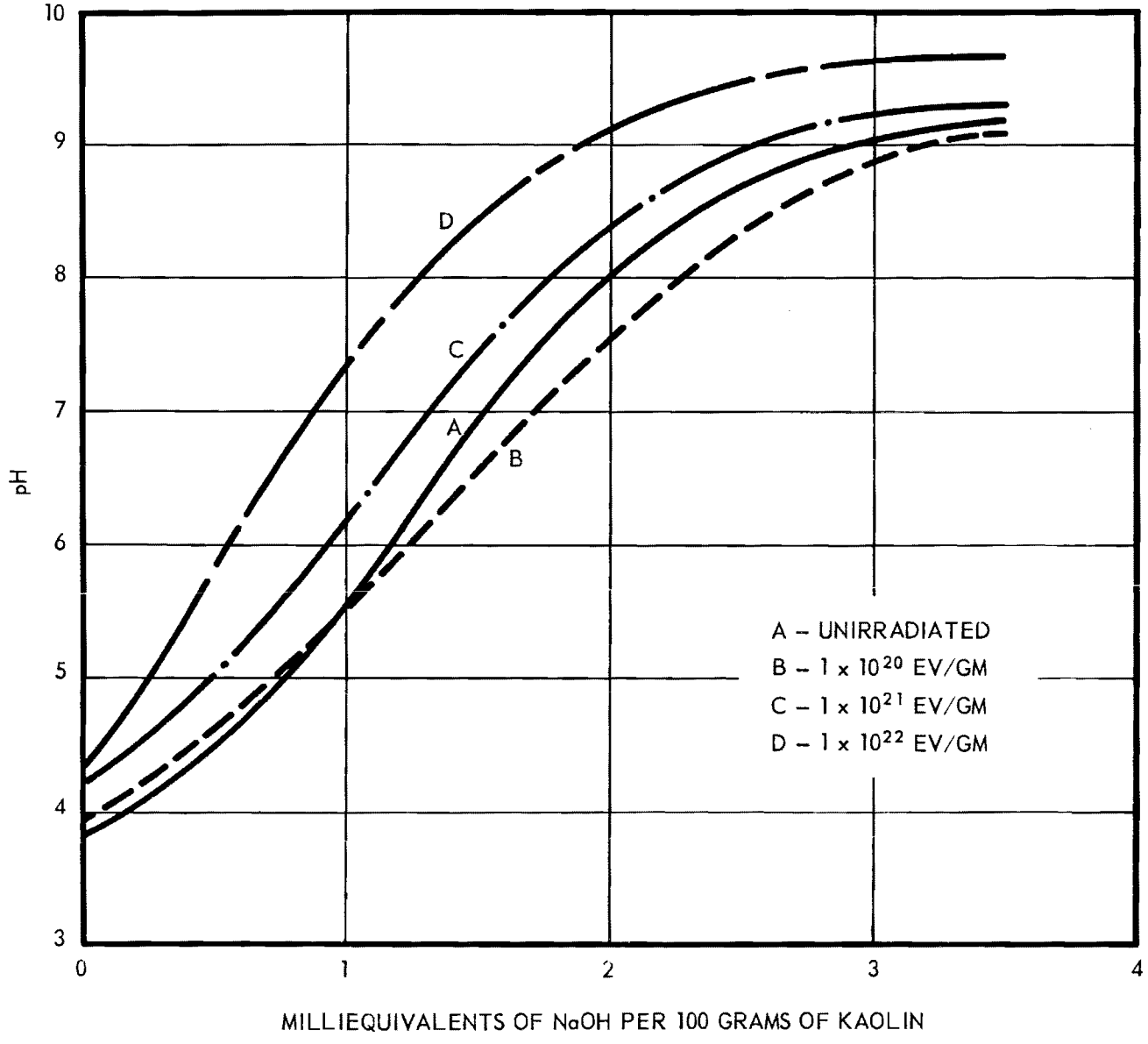


Figure 19. Titration Curves for Hydrogen-Kaolinite Prepared from Twiggs County Kaolin.

of the two unirradiated clays. Murray and Lyons[17] have shown that the cation-exchange capacity of a poorly crystallized kaolin is as much as four times that of a well crystallized kaolin. Therefore, the cation-exchange capacity of the Washington County kaolin which was very poorly crystallized should have been much greater than the Twiggs County kaolin. The fact that it was not is strong evidence that cation-exchange had taken place with the deflocculating agent.

I. Viscosity Determinations

Viscosity determinations were made on an unirradiated sample and two irradiated samples of Washington County kaolin. A slurry containing 55 per cent by weight of kaolin was prepared with 0.75 per cent solution of tetrasodium pyrophospate. The kaolin and tetrasodium pyrophosphate solution were blended in a Waring Blendor and agitated for 5 minutes. The temperature of the slurry was adjusted to 81° F and the apparent viscosity determined with a Brookfield viscometer, model LVF, at varying rates of shear. The data obtained are presented in Table III. These data show an increase in slurry viscosity with increasing radiation dose.

J. Reflectance Measurements

Light reflectance measurements were made on samples of the Washington County kaolin that had received various doses of gamma-radiation. The results of these measurements are presented in Table IV. The tests were made with a General Electric recording spectrophotometer. Approximately 10 grams of kaolin were pressed into a pellet 1-1/4 inches in diameter under a pressure of 60 pounds per square inch. The amount of incident light

[17] H. H. Murray and S. C. Lyons, "Further Correlations of Kaolinite Crystallinity with Chemical and Physical Properties," Eighth National Conference on Clays and Clay Minerals - Pergamon Press, 11-17 (1960).

TABLE III

APPARENT VISCOSITIES OF SLURRIES OF WASHINGTON COUNTY KAOLIN AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Spindle (Number)	Rate of Rotation (RPM)	Apparent Viscosity (Cps)
Unirradiated kaolin	2	12	40.0
	2	30	68.0
	2	60	89.5
1.0×10^{20}	2	12	80.0
	2	30	85.0
	2	60	100
1.0×10^{22}	2	12	113
	2	30	100
	2	60	104

TABLE IV

REFLECTANCE MEASUREMENTS FOR KAOLIN SAMPLES WITH VARIOUS TOTAL ENERGY DOSES

Wave Length (Millimicrons)	Per Cent Reflectance		
	Unirradiated	1×10^{21} EV/Gm	1×10^{22} EV/Gm
380	66.0	65.0	65.0
400	69.7	68.7	68.5
450	77.0	76.0	76.0
500	80.5	79.8	80.0
550	84.0	83.0	83.2
600	86.2	85.2	85.3
650	88.0	86.8	86.8
700	89.5	88.5	88.2

reflected from the surface between wave lengths of 380 and 700 millimicrons was measured relative to a similar size pellet of magnesium oxide. No detectable difference was observed in the reflectance as a function of radiation dose.

K. Grinding Studies

Samples of the Washington County kaolin, both unirradiated and irradiated, were subjected to 50 hours of wet-grinding. A porcelain mill 9 inches in diameter was used for this study. The mill was charged with 100 grams of sample, 3 kilograms of 3/4-inch diameter, 3/4 inch-length porcelain cylinders, and 400 grams of water. The milling speed was 120 revolutions per minute. Specific surface areas were determined for these samples after they had been ground. The technique used for these measurements was the same as outlined earlier in this report, and the results are contained in Table V.

A significant increase in specific surface areas was obtained for the irradiated kaolins. Since the grinding conditions were identical for these samples, the increase in specific surface area is a good indication that the kaolin is more easily ground with increasing radiation dose. Wet grinding, as opposed to dry grinding, produces more shearing forces than crushing forces. Therefore, the fine particles produced by wet grinding are predominantly plate-like as a result of shearing forces exerted along the cleavage planes of the crystallites comprising a stack.

TABLE V

SPECIFIC SURFACE AREAS OF WET-GROUND KAOLIN
AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area (M^2/Gm)
Unirradiated	26.7
1.0×10^{20}	27.8
1.0×10^{21}	28.8
1.0×10^{22}	31.1

III. DISCUSSION AND CONCLUSIONS

There are three possible mechanisms for the interaction of gamma-rays with matter: the photoelectric effect, the Compton effect and pair production. Of these three mechanisms the atomic cross-section for the Compton process is at least four times greater than the sum of the other two (that for pair production is zero at this energy) for the interaction of 0.667-Mev gamma-rays with the principal atoms comprising kaolinite. In the Compton process, electrons are ejected with an energy spectrum in which the maximum energy is comparable to the original gamma-ray energy, and thus the substance being irradiated is subjected to an internal bombardment of energetic electrons. Most of the energy of the beta-radiation (primary electrons) is dissipated in producing further ionization, but some atomic displacements are produced. The defects produced by this internal electron bombardment are of the simplest type: isolated interstitial vacancy pairs, which are called "close-Frenkel-pairs."[18] For a certain minimum separaration there is evidence that such defects are quite stable, and highly resistant to recombination, in covalent lattices. A covalent bond is formed from the hybridization of atomic wave functions in such a manner that two-electron links between atoms have a low energy for certain directions only. This more-or-less rigid directional property is the dominant factor which governs the behavior of covalent solids (i.e., hardness, resistance to cleavage, etc.). A vacancy or interstitial in such systems is therefore subject to an environment which behaves quite differently from that of a metal or ionic crystal. The neighboring atoms are more

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[18] D. S. Billington and J. H. Crawford, Jr., Radiation Damage in Solids (Princeton, New Jersey: Princeton University Press, 1961) p. 47.

rigidly fixed in position such that diffusion of the interstitial is somewhat unlikely, and bond rupture and reformation is necessary when an adjacent atom exchanges place with a vacancy. Therefore, the activation energy for motion of either defect is expected to be higher for a covalent crystal than that for a metal or ionic crystal with an equal cohesive energy.

The layer lattice of the kaolin minerals presents an unusual situation in that for the aluminum atoms only two-thirds of the available lattice sites are filled. As pointed out in the Introduction, this condition is necessary from the standpoint of valency. However, an aluminum atom that had been displaced from its normal lattice site could occupy one of these vacant sites even though its energy state in this new location might be considerably higher than that in its initial location. As has also been pointed out previously, one of the criteria for crystal perfection in kaolinite is the degree to which the arrangement of aluminum atoms in successive layers is duplicated. The X-ray diffraction results definitely indicate that this order is decreased by gamma-radiation. The aluminum atoms in the layer lattices are apparently being displaced from their original sites in a random fashion and thus producing the effect that the various layers had been displaced by $nb_o/3$ shifts with respect to one another. Since any aluminum atom is surrounded by three immediately adjacent vacant sites, these displaced atoms may not necessarily remain as interstitials. They may instead fall into one of the vacancies. In either case, the effect is one of producing randomness in the aluminum positions which will appear in the X-ray diffraction pattern. The situation with the remaining atoms comprising the kaolin layer is the

same as that for any common crystal lattice with all available lattice sites being filled except for vacancies arising from growth defects. In the remainder of the lattice the atoms most likely to be displaced are the silicon atoms and the oxygen atoms. In the silica tetrahedra each silicon atom is surrounded by four oxygen atoms, and each oxygen, in turn, is shared by adjoining tetrahedra, thereby forming a complex network array. Hence, only two bonds need to be broken to displace any oxygen while four bond ruptures are needed to displace a silicon atom. In addition, many of the oxygens need be displaced only short distances (≈1 angstrom) to find a relatively large interstitial void.

From the foregoing discussion it can be seen that the decrease in the crystallinity of kaolinite can be evaluated in terms of two separate mechanisms: the increase in the apparent $nb_o/3$ shifting and the production of interstitial-vacancy pairs in the lattice. The index of $nb_o/3$ crystallinity is presented in Figures 14 and 15, while the data of Figure 16 are a measure of the total number of interstitial-vacancy pairs that are formed. It is interesting to note that in both these plots the crystallinity of the samples appears to become better from the lowest irradiation dose up to a point and then decreases. That is, the index of $nb_o/3$ crystallinity in Figures 14 and 15 appears to become higher and the total number of interstitial-vacancy pairs, as indicated in Figure 16, becomes less. For doses greater than 10^{19} electron-volts per gram the crystalline order becomes progressively worse, as would normally be expected from radiation damage.

Since nothing is known concerning the rates of displacement or recombination for either of these systems, any firm interpretation of the critical points in these curves is not possible. One interesting point is

that the residence time for a dose of approximately 1 x 10^{19} electron-volts per gram corresponds very closely to the time required for the sample temperature to reach a constant value.

Some of the changes in physical properties that have been observed in this work can be explained on the basis of the interstitial atoms produced by the gamma-radiation. The lattice vacancies within the layers cause a marked alteration in vibrational frequencies in their vicinity and the interstitial atoms will cause a buckling of the adjacent lattice layers which will change the vibration frequencies in this region. The effects should produce an increase in the interlayer or c_o lattice spacing. Unfortunately, time and funds would not permit additional X-ray diffraction studies necessary to measure this increase in lattice spacing. However, the delamination of stacks, the decrease in specific surface area and the apparent reduction in the amount of hydrogen bonding are probably all a direct result of the production of interlattice atoms and vacancies. The layer lattices of kaolinite are known to be held together by long hydrogen bonds and van der Waal's forces. The latter decrease in strength with the square of separation distance and Hendricks[19] has pointed out that the key feature of the interlayer coordination is the manner in which oxygens and hydroxyls approach one another in pairs to form long hydrogen bonds. Therefore, any interlayer distortion produced by interlattice atoms would tend to reduce both of these interlayer binding forces. Indeed, the results of the infrared adsorption studies with the Washington County

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[19] S. B. Hendricks, "The Crystal Structure of Nacrite and the Polymorphism of the Kaolin Minerals," Zeit Krist 100, 509-18 (1938).

kaolins indicate a possible reduction in the degree of interlattice hydrogen bonding. Within the normal kaolin layer, the silicon tetrahedral layers show considerable distortion from their idealized geometry, indicative of the strong interlayer forces between them.[20,21] The nature of these distortions are tension in the octahedral layer and compression of the silica sheet. It is very likely that a reduction in the interlayer binding forces between lattice layers by the presence of interlayer atoms would promote a relaxation of these stresses in adjacent faces. This would lead to a complete misfit between the layers and a severe reduction in the interlayer binding forces. This effect is probably responsible for the production of small particles observed for the Twiggs County kaolin. Significant increases in particle concentration of the irradiated and fractionated Twiggs County kaolin begin to appear at approximately 10 cubic microns particle volume. Koenig and Lyons[22] have reported that individual kaolin plates begin to appear at approximately 2 microns, equivalent spherical diameter. Although a direct correlation of these two observations is not possible, it is obvious that the first manifestation of change in the irradiated Twiggs County kaolin is in the same size range as the first appearance of individual kaolins plates. This is a very significant result. It indicates that these small particles are being produced by a delamination process. Any comminution process

[20] L. C. Pauling, "The Structure of Micas and Related Minerals," Natl. Acad. Sci. Proc. 16, 123-129 (1930).

[21] R. E. Newnham, "A Refinement of the Dickite Structure and Some Remarks on Polymorphism in Kaolin Minerals," Mineral. Mag. 32, 683-704 (1961).

[22] Koenig and Lyons, Loc. cit.

graually reduces all the particles in a sample to smaller and smaller sizes until the desired size distribution is reached. However, the reduction of particle size occurring by the effect of high-energy, ionizing radiation seems to produce particles by the delamination or "flaking off" of plates of a size below 2 microns equivalent spherical diameter rather than continuously reducing the size of all the particles by a proportional amount. This could account for the fact that no difference can be detected in the size distributions for the larger particles which are stacks of plates. Many small plates of the size represented in the range below 2 microns would have to be removed from a large stack of plates before any change in the apparent volume of the stack would be detectable. If all the stacks in a sample of one of the clays studied were to have one plate delaminated from each stack, an increase in the number of very small particles such as found for Twiggs County kaolin would be possible without any detectable changes in the size of the stacks. Even if the delamination process is not this uniform, quite a few plates would have to be removed from a large number of stacks before a detectable change in the upper portion of the size distribution would occur. A size reduction of the stacks will become noticeable only when a greater degree of delamination is obtained than has been accomplished in this work, or by using a sample of clay in which the sizes of the stacks are smaller so that the removal of one or two plates from a significant percentage of these stacks will produce a detectable change in the overall size distribution.

Both the Washington County kaolin and the Twiggs County kaolin contained a great number of stacks. However, delamination was found for

the Twiggs County kaolin and none for the Washington County kaolin. A careful examination of the nature of the stacks present in the Washington County kaolin and Twiggs County kaolin (Figures 3 and 4, respectively) reveals a significant difference. The stacks of the Washington County kaolin are composed of many very small crystallites whose length and breadth are much smaller than the dimensions of the stacks perpendicular to the axis of preferred orientation, and the stacks have a very tightly packed appearance. There appears to be considerable overlapping of the crystallites within a single layer of the stack, which indicates some bonding between the edges of adjacent crystallites, and certainly points to physical interference to the removal of any one crystallite even if its interlayer forces were reduced. The situation with the Twiggs County kaolin, however, is quite different. The individual crystallites comprising the stacks in this kaolin appear to have a length and breadth equal to the dimensions of a stack perpendicular to the axis of preferred orientation. Therefore, a layer or laminate of one of these stacks is a single crystallite rather than a number of small crystallites. Also, the individual stacks appear to be smaller with a more loosely pack and flaky appearance. This difference in structure is also reflected in the observed difference in the crystallinity of the two unirradiated kaolins. This difference in crystalline arrangement probably accounts for the fact that delamination was observed for the Twiggs County kaolin, and not for the Washington County kaolin. A crystallite on the surface of one of the stacks in the Twiggs County kaolin would meet no further resistance to flaking off once the interlayer binding forces were reduced, while a crystallite in a surface layer of a stack in the Washington County kaolin

would receive hindrance from overlapping adjacent crystallites and edge bonding with adjacent crystallites. The relatively low crystallinity of the Washington County kaolin may also be an indication that the tensile and compressive forces between adjacent alumina and silica sheets may not be so pronounced due to the poor order present initially and further disorder produced by irradiation causes very little relaxation for promoting delamination.

A clear explanation for the observed reduction in the specific surface areas of the two kaolins is not possible on the basis of the information available. At least two explanations are possible, and further experimental work would be necessary to arrive at any definite conclusions. The most probable explanation is that the buckling and distortion of the lattice layers caused expansion into the cracks and crevices between the crystallites at the surface of the stacks. This effect was found to be responsible for the reduction in specific surface area of artificial graphites, a layer lattice material, upon exposure to neutron irradiation.[23] Another explanation could be that the gamma-radiation alters the surface properties of the kaolin. The electron micrographs presented in Figures 5, 6, 7, 8, and 9 suggest that the surfaces of the stacks are altered quite significantly by the gamma-radiation, particularly in the case of Figures 7, 8, and 9 where the surfaces have developed a vitrified appearance. However, less than about 20 per cent of the stacks examined exhibited such radical surface alteration, and the effect was observed less frequently for the irradiated samples of Twiggs County kaolin where a more significant

[23] C. N. Spalaris, L. P. Bupp, and E. C. Gilbert, "Surface Properties of Irradiated Graphite, J. Phys. Chem. 61, 350-54 (1957).

amount of alteration would actually be needed to overcome the increase in specific surface area due to the small plates produced by delamination.

An explanation for the surface change noted in some of the kaolin stacks after irradiation is not available. As already mentioned, some surfaces exhibit a vitreous appearance that is not observed, at least to the knowledge of these investigators, in a normal, unirradiated kaolin. It is expected that the production of such a condition would require local temperatures far in excess of the bulk temperature observed during irradiation. The surfaces seem to have been etched by some means as ridges and pits of considerable size are visible on the edges of the stacks. Surface irregularities of this size arising from the diffusion of interstitials and vacancies to the surface seems quite unlikely. An interesting factor is that this etching was observed only for the Washington County kaolin. It is quite conceivable that this surface behavior is responsible for the increase in cation-exchange capacity observed for the Washington County kaolin. Since cation-exchange in kaolinite is due primarily to broken bonds[24] and to negative charges on the lattice due to vacancies of aluminum or silica positions, the etching may have exposed more sites for cation-exchange. The Washington County kaolin, as has been pointed out previously, was treated with a sodium pyrophosphate deflocculating agent before the material was selected for irradiation studies. This probably accounts for the subsequently measured, low cation-exchange capacity of the unirradiated material for sodium, and it is possible that the etching is a result of the initial sodium-exchange. In

[24] S. Spiel, "Affect of Adsorbed Electrolytes on Properties of Monodispersed Clay-Water Systems," J. Am. Cer. Soc. 23, 33-38 (1940).

the presence of the radiation field this sodium may have combined with oxygen from the lattice to form an oxide of sodium which then dissolved when the kaolin was dispersed in water prior to being deposited on the electron microscope grids. The etch effect would then be a result of the removal of oxygen atoms from the kaolinite lattices. This in turn would make more sites available for cation-exchange for the irradiated material. The above hypothesis could account for the difference in surface etching and cation exchange capacity noted for the two kaolins used in this study. The lowering of the cation-exchange capacity for the irradiated Twiggs County kaolin is probably due entirely to the observed decrease in surface area which blocked off some of the sites normally available for cation-exchange.

The measurements of slurry viscosity for the Washington County kaolin produced some very interesting results. It has been demonstrated that a significant correlation exists between the kaolinite crystallinity and the viscosity of a slurry of the material.[25,26] This correlation was thought to exist principally because poorly crystallized kaolins usually contain smaller particles than well-crystallized ones, and the higher viscosity was a result of the friction of the many more edges and corners available; although the possibility of the presence of a greater concentration of valence forces to provide a higher electrokinetic component of viscosity was recognized. Since no significant reduction in particle

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[25] H. H. Murray and S. C. Lyons, "Correlation of Paper-Coating Quality with Degree of Crystal Perfection of Kaolinite," Proc. Fourth Natl. Conf. on Clays and Clay Minerals - National Research Council Pub. 456, 31-40 (1956).

[26] Murray and Lyons, Loc. cit.

size was detected for the Washington County kaolin while a significant increase in the viscosity with increasing radiation-dose was observed, it appears that the observed viscosity increase was due to an electrokinetic effect arising from a greater number of valence forces in the irradiated material.

The data from the wet-grinding of the Washington County kaolin after irradiation provide further support for the discussion of weakening interlayer forces presented earlier. Since wet-grinding provides primarily shearing forces, any reduction in the strength of the interlayer binding forces would be expected to result in a greater degree of size reduction for equal energy input. Using the specific surface area of the ground material as a measure of the degree of size reduction, this is exactly what was observed. Unfortunately, time limitations did not permit the direct measurement of particle sizes resulting from the wet-grinding experiments.

Since the nature of this research program has been primarily exploratory, and the experiments have of necessity been limited to two kaolins, some of the conclusions drawn from this work are necessarily quite tentative. The conclusions that can be drawn are:

(1) Lattice defects of isolated interstitial-vacancy pairs, which are stable at room temperature, are produced in the kaolinite lattice by the effect of 0.667-Mev gamma-rays.

(2) Some physical surface alteration is produced on the kaolinite crystallites by the gamma-radiation used in this work. A portion of the alteration observed may be due to a chemical process--with adsorbed cations--initiated by the gamma-radiation.

(3) The interlattice bonding forces of the kaolinite appear to have been reduced due to interlattice atoms produced by the gamma-radiation.

(4) Delamination of kaolinite crystallites may occur from the stacks as a result of this weakening of interlayer bonding. Whether or not delamination does occur appears to depend on the presence of other hindrances, i.e., overlapping crystallites, edge bonding between crystallites in the same layer, etc. The initial degree of crystallinity may also be an important factor.

(5) The specific surface area of kaolin is reduced by the effect of gamma-radiation.

(6) The cation-exchange capacity of a raw, untreated, kaolin is reduced by the effect of high-energy, ionizing radiation. This is probably due to the blocking off of available exchange sites by whatever mechanism is reducing the specific surface layer.

(7) The slurry viscosity of an irradiated kaolin is greater than for the unirradiated kaolin and the viscosity increases with increasing radiation dose. This effect is apparently an electrokinetic one arising from a greater number of valence forces in the irradiated material.

(8) The ease with which kaolin can be wet-ground is enhanced by exposure to gamma-radiation.

IV. RECOMMENDATIONS

The exploratory nature of this research project has uncovered a number of points that justify further investigation and has suggested other areas that warrant research. In general, the investigations performed during the course of this research should be extended to include at least five or six more kaolins from various sources and possessing diverse physical properties (i.e. particle size, specific surface area, degree of crystallinity) to provide a more firm foundation for acceptance or rejection of the conclusions drawn from this work. In addition, some of the more specific points that appear to warrant extensive investigation are:

(1) The examination of individual stacks of kaolin exposed to varying doses of gamma-radiation. This could be accomplished by depositing single stacks on electron microscope grids, and irradiating the stacks without removing them from the grids. This would allow examination, by electron microscopy and electron diffraction, of individual stacks and thereby eliminate some of the statistical fluctuations due to sampling that were undoubtedly encountered here.

(2) The examination of the effect of crystal orientation within a unidirectional radiation field on the amount and type of damage produced by high-energy, ionizing radiation may be dependent upon crystal orientation.

(3) Examination of the increase in c_o spacing produced by the presence of interlattice atoms. This could be accomplished with X-ray diffraction traces using a scale with sufficient

expansion to detect small changes in the Bragg angle of the 001, 002, or 003 diffraction maximum.

(4) Preheating of the samples to 100° F before introducing them into the Research Irradiator to ascertain whether or not the apparent reduction in radiation damage observed for the lower radiation doses is actually due to the rise in sample temperature during irradiation.

(5) Careful examination of the pore volumes of kaolin samples before and after exposure to gamma-radiation. This work would help to establish exactly the nature of the mechanism that reduces the specific surface area during irradiation. For this work kaolins with a wide range of initial surface area should be employed.

(6) Irradiation and subsequent examination by electron microscopy of kaolins with and without exchanged cations to determine whether or not the surface etching observed in this work is a chemical effect.

(7) Examination of the extent of delamination produced by neutron irradiation. Due to the more extensive damage of the displacement type produced by neutron irradiation, the degree of delamination of kaolin stacks might be much greater.

(8) More precise and extensive investigations of the infrared adsorption spectra of kaolins as a function of radiation dose. Information of this type would be very valuable in establishing the exact nature of the structural disorder produced by the gamma-radiation.

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